IN THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF DELAWARE

CALLAWAY GOLF COMPANY,)
Plaintiff,) C.A. No. 06-91 (SLR)
v.) PUBLIC VERSION
ACUSHNET COMPANY,)
Defendant.)

ACUSHNET'S OPPOSITION TO CALLAWAY'S MOTION TO EXCLUDE PRIOR ART TESTING EVIDENCE

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I. INTRODUCTION

Callaway's motion to exclude the testimony of Dr. MacKnight, while styled as a *Daubert* motion, is at its core a motion *in limine* seeking to exclude evidence of testing of balls made according to the prior art references. This testing, however, is highly probative of what would have been known, or ascertainable, to a person of ordinary skill in the art without undue effort or experimentation. These balls, made from the express teachings of the prior art, provide strong evidence that it would have been obvious to make the balls of the asserted claims, even under Callaway's flawed claim construction.

There is no dispute that the Proudfit prior art patent teaches every single element of the asserted claims of the patents-in-suit except the use of polyurethane. Moreover, the use of polyurethane as a cover layer of a golf ball is unambiguously and indisputably taught in the prior art Wu and Molitor patents. The prior art *explicitly teaches* the combination of polyurethane as the outer cover of balls like Proudfit. Thus, the balls made following the teaching of Proudfit, combined with a polyurethane outer cover taught by the other prior art, represent what a person of ordinary skill would have made simply by following the instructions of the prior art. Courts routinely admit evidence of testing performed in accordance with the teaching of the prior art. The Federal Circuit has even chastised parties for not undertaking to conduct such tests.

Callaway's position borders on the absurd. Callaway contends that, to invalidate the patents-in-suit, Acushnet must demonstrate the "on the ball" Shore D hardness of the cover layers in the prior art. But at the same time, Callaway's motion seeks to exclude un-rebutted "on the ball" measurements of the hardness of the cover layers of balls taught in the prior art. Callaway's ill-considered, opaque attempt to insulate its patents from the inevitable finding of invalidity should fail.

Callaway's argument that none of the exact balls that were tested existed in 1995 misses the point. The ball testing demonstrates what a person of ordinary skill could learn from the routine task of making and testing the balls that were taught in the prior art. As the Supreme

Court recently made clear, a person of ordinary skill "is also a person of ordinary creativity, not an automaton." See KSR Int'l Co. v. Teleflex Inc., 127 S.Ct. 1727, 1742 (2007) ("Common sense teaches [that] in many cases a person of ordinary skill will be able to fit the teachings of multiple patents together like pieces of a puzzle."). It is therefore well within the ordinary skill of an artisan to follow the express teachings of the prior art and to measure the properties of the

resulting balls.

The testing here does just that, and is admissible.

Callaway's attack on Dr. MacKnight's testimony, apart from the admissibility of the balls themselves, also should fail. The touchstone for admissibility of expert testimony is whether the expert's technical or specialized knowledge would assist the trier to understand the evidence or determine an issue of fact. Here, Dr. MacKnight is a material sciences expert of unassailable credentials who supervised and approved the entire process of making and testing the balls at issue. That he did not personally make the tested balls, or personally perform the Shore D testing, and instead relied on lab technicians that he instructed, does not matter. Such expert reliance on lab technicians is commonplace, and wholly appropriate to support expert testimony. Dr. MacKnight's testimony easily passes the test for admissibility of expert testimony.

II. NATURE AND STAGE OF PROCEEDINGS

Callaway alleges that Acushnet infringes the patents-in-suit. Acushnet disputes this and contends that the patents-in-suit are invalid. A two-week jury trial is scheduled to begin on December 3, 2007. However, the parties have filed several motions for summary judgment related to the invalidity of the patents-in-suit, and oral argument on those motions, and on claim construction, is scheduled for September 28, 2007.

III. FACTUAL BACKGROUND

A. The Patents-in-Suit

In general, the patents-in-suit¹ describe and claim a golf ball comprising three components: a core; an inner cover layer; and an outer cover layer. Acushnet provided a background of the patents-in-suit in earlier filings, and does not repeat that description here. [D.I. 216, at 3-6]. However, one aspect of the asserted claims is relevant to this motion.

Each of the asserted claims recites a limitation on the "Shore D hardness" of one or both of the cover layers. Generally speaking, the asserted claims require the inner cover layer to have a Shore D hardness of 60 or more, and the outer cover layer to have a Shore D hardness of 64 or less.² The parties dispute how the "Shore D hardness" limitations should be construed. Acushnet asserts that Shore D hardness must be measured in accordance with ASTM D-2240 (the measurement standard set forth in the patents-in-suit), which requires an "off the ball" measurement of a slab of material. Callaway asserts that the Shore D hardness must be measured "on the ball," which is not in accordance with the ASTM D-2240 standard. The parties have briefed their respective positions on this claim construction issue. [D.I. 204, 207, 262, 260].

B. The Prior Art

The golf balls of the asserted claims are explicitly taught and suggested in several key pieces of prior art. Acushnet set forth in detail why the asserted claims are obvious and anticipated in light of this prior art in its motion for summary judgment of invalidity. [D.I. 217].

¹ U.S. Patent Nos. 6,210,293 ("the '293 patent"); 6,506,130 ("the '130 patent"); 6,503,156 ("the '156 patent"); and 6,595,873 ("the '873 patent") (collectively "the patents-in-suit").

² These limitations are formulated somewhat differently in each of the asserted claims. In particular, each asserted claim recites an inner cover having a "Shore D hardness of 60 or more," "Shore D hardness of about 60 or more," or "Shore D hardness of at least 60." In addition, each asserted claim other than claims 4, 6-8, and 10-11 of the '156 patent recites an outer cover having a "Shore D hardness of 64 or less" or "Shore D hardness of about 64 or less."

A brief review of the prior art combinations that Acushnet relies on is relevant to Callaway's motion.

The Proudfit reference teaches every limitation of the asserted claims other than the use of polyurethane. Specifically, Proudfit teaches a three-piece, dual cover layer golf ball with the following components:

- a core;
- an inner cover layer that is a blend of low-acid ionomers, with a thickness of 0.037 inches, and a Shore D hardness greater than 60; and
- an outer cover layer that is a blend of synthetic balata and polybutadiene, with a thickness of 0.0525 inches, and a Shore D hardness less than 64.

Ex. 2, Proudfit at col. 7:35-47; 8:25-30; 8:45-55.³ In addition, the use of polyurethane as a golf ball cover material was widely known by 1995, and is specifically taught in the Molitor '751, Wu, and Molitor '637 patents. Thus, there is nothing new in the patents-in-suit.

Moreover, the asserted prior art explicitly teaches using polyurethane on a ball like that described in Proudfit. Specifically, the Molitor '751 patent describes applying a polyurethane/ionomer blended cover to "balls having a separate solid layer beneath the cover as disclosed, for example, in U.S. Patent No. 4,431,193 to Nesbitt...." Ex. 3, Molitor '751 at col.

3:9-11 Likewise, Wu explicitly teaches to replace

ionomer and balata cover materials with its polyurethane cover material:

It has been proposed to employ polyurethane as a cover stock for golf balls because, like SURLYN®, it has a relatively low price compared to balata. However, unlike SURLYN®-covered golf balls, polyurethane-covered golf balls can be made to have the "click" and "feel" of balata.

³ As set forth in detail in Acushnet's motion for summary judgment, Nesbitt similarly teaches a three-piece solid construction ball. [D.I. 217 at 23-29].

Ex. 4, Wu at col. 1:40-43. Thus, Proudfit, in combination with any of the polyurethane references, renders obvious the asserted claims.

C. The Testing of Balls Taught by the Prior Art

Faced with the clear invalidity of the patents-in-suit over the Proudfit combinations, Callaway argues that the Shore D hardness of the cover layers must be measured "on the ball" rather than by using the ASTM D-2240 method. [D.I. 244, at 21]. Callaway cannot dispute the obviousness of the asserted claims under a proper construction that embraces measuring Shore D hardness as required by ASTM D 2240. [See D.I. 207 at 10-20].

Specifically, Dr. MacKnight made balls that were taught by the Proudfit combinations and the Nesbitt combinations. The Proudfit combination balls (BALL_7, BALL_8, and BALL_9 in Dr. MacKnight's report) were made precisely to the specifications of Proudfit, with the outer cover replaced by the polyurethane described in the polyurethane references. *Id.* at ¶¶ 23-25. The Nesbitt combination balls (BALL_1 – BALL_6) were made precisely to the specifications of Nesbitt, with the inner and/or outer cover layer replaced as indicated. *Id.* at ¶¶ 17-22. The only component of the Nesbitt combination balls that was not explicitly taught by Nesbitt was the core composition.⁴ Nesbitt teaches only the use of a solid rubber core, without specifying the precise core composition. Ex. 5, Nesbitt, col. 3:26-30; col. 4:18-6:27. Thus, Dr. MacKnight used a core composition that was typical of core compositions at the time, and is the composition that the patents-in-suit attribute to the Nesbitt patent. *Id.* at ¶ 8; '293 patent, col.

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⁴ Nor is any particular core recipe claimed by the patents-in-suit.

18:30-34; 19:3-5; 20:10-12. While this core composition is not explicitly described in Nesbitt, it is certainly consistent with its description.

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If there were any doubt as to whether the balls were made precisely according to Dr. MacKnight's instructions, Mr. Dalton would testify that they were. Mr. Dalton, who has been designing and making golf balls since 1989, personally supervised the creation of the materials and balls according to the prior art, and personally ensured that they were made according to Dr. MacKnight's instructions, and would so testify. Ex. 6, Dalton Decl. ¶ 8. Mr. Dalton was also present when the balls were provided to the private accredited testing lab (PTLI) for testing, and when PTLI personnel were instructed on what tests to perform, and would testify to that as well. *Id.* at ¶ 10-14. Mr. Dalton also received the test results from PTLI. *Id.* at ¶ 15.

Thus, regardless of whether Dr. MacKnight's testimony is admitted, which it should be, the ball testing evidence itself, and Mr. Dalton's testimony regarding the construction and testing of the golf balls is independently admissible.

IV. LEGAL STANDARDS

A. Admissibility of Prior Art Testing Evidence

The admissibility of prior art testing evidence, like any other factual evidence, is governed by the Federal Rules of Evidence. Under Rule 402, relevant evidence is admissible. Under Rule 401, evidence is relevant if it has any tendency to make a material fact more or less probable.

Courts routinely admit testing of items made in accordance with the teachings of prior art, as relevant to the issues of obviousness and invalidity. See, e.g., Young Dental Mfg. Co., Inc. v. Q3 Special Prods., Inc., 112 F.3d 1137, 1146 (Fed. Cir. 1997) (affirming District Court's decision to admit models made according to the teachings of the prior art even when the models "oversimplified" the prior art). See also Ciba-Geigy Corp. v. Alza Corp., 864 F. Supp. 429, 436-39 (D.N.J. 1994) (considering as evidence of invalidity expert experimentation according to the teachings of a prior art reference and finding asserted claims invalid); ADM Corp. v.

Speedmaster Packaging Corp., 384 F. Supp. 1325, 1345 (D.N.J. 1974) ("This Court has considered numerous patents, and models made from those patents, in seeking to find the prior art against which to judge the obviousness of Beskind's claimed invention."); Cardinal of Adrian, Inc., v. Peerless Wood Prods., Inc., 363 F. Supp. 1298, 1300 (E.D. Mich. 1973), aff'd, 515 F.2d 534 (6th Cir. 1975) ("The Court also observed demonstrations of assembled kitchen cabinets equipped with such hinges and studied working models of other hinges which defendants had built pursuant to the disclosures of certain prior art patents.").

The touchstone for the admissibility of such testing, as governed by Rule 401, is whether it has a tendency to make the fact in question (in this case the obviousness and/or inherency of certain features of golf balls described by the prior art) more or less probable. Fed. R. Evid. 401.

B. Admissibility of Expert Testimony

The admissibility of Dr. MacKnight's testimony, as distinct from the prior art testing evidence itself, is governed by the Federal Rules of Evidence. Rule 702 reads as follows:

If scientific, technical or other specialized knowledge will assist the trier of fact to understand the evidence or to determine a fact in issue, a witness qualified as an expert by knowledge, skill, experience, training, or education, may testify thereto in the form of an opinion or otherwise, if (1) the testimony is based upon sufficient facts or data, (2) the testimony is the product of reliable principles and methods, and (3) the witness has applied the principles and methods reliably to the facts of the case.

Fed. R. Evid. 702.

Rule 702 imposes three requirements on expert testimony: "qualification, reliability, and fit." See, e.g., Schneider v. Fried, 320 F.3d 396, 404 (3d Cir. 2003). "Qualification refers to the requirement that the witness possess specialized expertise." *Id.* The Third Circuit has "interpreted this requirement liberally, holding that 'a broad range of knowledge, skills, and training qualify an expert." *Id.* (citations omitted). The second requirement of reliability

means that "the expert must have 'good grounds' for his on [sic] her belief." Id. In determining whether testimony is reliable, courts in the Third Circuit⁵ examine several factors:

(1) whether a method consists of a testable hypothesis; (2) whether the method has been subject to peer review; (3) the known or potential rate of error; (4) the existence and maintenance of standards controlling the technique's operation; (5) whether the method is generally accepted; (6) the relationship of the technique to methods which have been established to be reliable; (7) the qualifications of the expert witness testifying based on the methodology; and (8) the non-juridical uses to which the method has been put.

Calhoun v. Yamaha Motor Corp., U.S.A., 350 F.3d 316, 321 (3d Cir. 2003) (quoting In re Paoli R.R. Yard PCB Litig., 35 F.3d 717, 742 n.8 (3d Cir. 1994)). However, these factors are neither exclusive nor mandatory, and should be examined by the court if they are relevant to the particular facts at hand. Izumi Prods. Co. v. Koninklijke Philips Elecs. N.V., 315 F. Supp. 2d 589, 601 (D. Del. 2004), aff'd, 140 Fed. Appx. 236 (Fed. Cir. 2005). Fit requires that the "expert's testimony must be relevant for the purposes of the case and must assist the trier of fact." Id.

If the expert is qualified, and the testimony is based on reliable methodology and is relevant to the case, it should be admitted. Questions about the expert's methodology that do not impact the reliability or relevance of his testimony go to the weight of the testimony, and do not affect the admissibility of the testimony. See Feit v. Great-West Life & Annuity Ins. Co., 460 F. Supp. 2d 632, 640, 41 (D.N.J. 2006) (citing Heller v. Shaw Indus., Inc., 167 F.3d 146, 152 (3d. Cir. 1999) ("An expert opinion is not inadmissible because it may contain flaws")); see also Polymer Dynamics, Inc. v. Bayer Corp., No. 99-4040, 2005 U.S. Dist. LEXIS 7945, at *12 (E.D. Pa. May 2, 2005) ("Any differences between the experiment of Dr. Johnson and the actual operation of the Bayer machinery goes to the weight of Dr. Johnson's testimony, not its admissibility.").

⁵ Third Circuit law governs the admissibility of expert testimony. See Ecolab, Inc. v. Amerikem Labs., Inc., 98 F. Supp. 2d 569, 576 n.13 (D.N.J. 2000) (citing Odetics, Inc. v. Storage Tech., Corp., 185 F.3d 1259, 1276 (Fed. Cir. 1999)).

V. ARGUMENT

A. The Testing of the Proudfit Combination Balls is Highly Probative, Admissible Evidence of Obviousness

The balls made according to the Proudfit combinations⁶ are probative of what one of ordinary skill in the art in 1995 would have recognized from the teaching of the prior art. As the Supreme Court recently held, "[a] person of ordinary skill is also a person of ordinary creativity, not an automaton." *KSR*, 127 S.Ct. at 1742. Thus, it would have been well within the ordinary skill of such a person to make a golf ball using the teaching of the prior art.

Proudfit discloses a three-piece ball that has all of the characteristics of the patents-insuit, with the exception of the use of a polyurethane outer cover layer. Ex. 2, Proudfit col. 7:35-47; 8:25-30; 8:45-55. The polyurethane references, in particular the Molitor '751 and Wu patents, expressly teach one skilled in the art to replace the outer cover of three-piece balls, like the Proudfit ball, with polyurethane. Ex. 3, Molitor '751 at 3:9-11; Ex. 4, Wu at 1:40-43. All Dr. MacKnight did is follow those express teachings to create the Proudfit ball with the outer cover replaced by the polyurethane of Molitor '751, Wu, and Molitor '637.

Notably, Callaway does not take issue with any of the specific materials or dimensions used to create the Proudfit combination balls. Indeed, it could not, since Proudfit specifies precise thicknesses and materials, to which the tested balls scrupulously adhered. Also, Callaway has offered no evidence that contests Acushnet's measurements of the tested balls,

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⁶ The balls made according to the Proudfit reference, in combination with Molitor '637, Wu, and Molitor '751, are specifically identified in Dr. MacKnight's declaration as BALL_7, BALL_8, and BALL_9 respectively. Ex. 7, MacKnight Decl. at ¶¶ 23-25. These balls are referred to herein as the "Proudfit combination balls."

which demonstrate that the tested balls have outer cover layer "on the ball" Shore D hardnesses well within the asserted claims of the patents-in-suit (well below 64 Shore D hardness).⁷

Thus, Callaway is left to argue only that the Proudfit combination balls are "irrelevant" because they were not available in 1995. [D.I. 282, at 6]. Callaway's desperate attempt to exclude this evidence should be rejected. The Proudfit combination balls that were made were expressly taught by Proudfit, in view of the polyurethane references, which expressly suggest using polyurethane in a ball like that of Proudfit. As such, they are probative of what one of ordinary skill in the art could readily ascertain in 1995.

Moreover, Callaway incorrectly insists that Acushnet is relying on principles of inherency to support its obviousness case with respect to the Proudfit combinations. [D.I. 282, at 10-11]. Callaway is wrong. Inherency is a term generally associated with anticipation under 35 U.S.C. § 102. Acushnet instead contends that the testing of the Proudfit combination balls show that a skilled artisan, applying no more than ordinary skill, would find it obvious upon making the balls expressly taught in the references, to make a ball that has such a Shore D hardness. Acushnet does not need to show inherency. See IXYS Corp. v. Advanced Power Tech., Inc., 321 F. Supp. 2d 1133, 1151 n.16 (N.D. Cal. 2004) ("IXYS argues at various points that a prior art reference must 'necessarily' or 'inherently' require the claim element that is believed to have been rendered obvious.... A [party] who seeks to prove invalidity for obviousness need not meet so stringent a standard") (citing Al-Site Corp. v. VSI Int'l, Inc., 174 F.3d 1308, 1323 (Fed. Cir. 1999)).

Courts regularly admit and rely on evidence of items that have been made generally in accordance with the teaching of the prior art, as evidence of invalidity. For example, in Young Dental Mfg. Co., the Federal Circuit affirmed the admissibility of such evidence to show obviousness. 112 F.3d at 1146. At trial, the defendant offered into evidence a model of an

⁷ For example, the Proudfit/Molitor '751 balls had an average measured "on the ball" Shore D hardness of 51.2, and the Proudfit/Wu balls had an average measurement of 56.8. Ex. 7, MacKnight Decl. ¶ 33.

embodiment from a prior art patent to try to show that the asserted patent was obvious. *Id.* The plaintiff argued that the model was misleading and incomplete since it "lacked many parts necessary for the operation of the device." *Id.* at 1145. Nonetheless Federal Circuit affirmed the admissibility of the evidence, noting that the plaintiff had "ample opportunity to cross-examine the witness that relied on the model in an effort to lessen the model's evidentiary weight." *Id.* at 1146. In doing so, the Court upheld the trial court's determination that any potential prejudice was outweighed by the probative value of the evidence, under Fed. R. Evid. 403. *Id.*

Similarly, here, if Callaway has any complaints about how the Proudfit combination balls were made (it has raised none thus far), any such complaints go to the weight the evidence should be accorded rather than its admissibility. Hence, the prior art testing should be admitted. See also Ciba-Geigy Corp., 864 F. Supp. at 436-39 (considering as evidence of invalidity an experiment done by an expert in which he combined the teaching of a prior art along with his own knowledge to substitute nicotine for nitroglycerine in an existing transdermal patch); ADM Corp., 384 F. Supp. at 1345 (considering models made from prior art patent in making its determination of obviousness); Cardinal of Adrian, 363 F. Supp. at 1300 (considering "working models of other hinges which defendants had built pursuant to the disclosures of certain prior art patents"). In fact, the Federal Circuit has actually criticized a party for not making a device described in the prior art to help prove its invalidity case. Crown Operations Int'l, Ltd. v. Solutia Inc., 289 F.3d 1367, 1378 n.4 (Fed. Cir. 2002).

Callaway relies on a single case, Wesley Jessen Corp. v. Bausch & Lomb, Inc., 209 F. Supp. 2d 348 (D. Del. 2002), aff'd, 56 Fed. Appx. 503 (Fed. Cir. 2003), in support of its position that recreations of prior art are not admissible. Callaway's reliance on Wesley Jessen is misplaced. Not only is Wesley Jessen distinguishable on its facts, but the reasoning of the case strongly supports the admissibility of the testing of the Proudfit combination balls.

As an initial matter, Wesley Jessen did not exclude <u>any</u> testing evidence or testimony at all. Instead, the court, to which the case was tried without a jury, considered the prior art testing and determined merely that the testing was not clear and convincing evidence of anticipation. Id.

at 393. Wesley Jessen says <u>nothing</u> about the admissibility of prior art testing evidence or testimony at all. Nor does it address the relevance of such testing to obviousness.

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Further, the facts of *Wesley Jessen* are vastly different from the testing of the Proudfit combinations in this case. There, the expert initially made sample material that followed precisely the teachings of prior art patent to try to show anticipation through inherency, and the sample material did not meet the limitations of the asserted patent. *Id.* at 373. The expert then decided to modify the material by making substitutions that were nowhere suggested or taught in the prior art. *Id.* at 373, 393. Eventually, he was able to make two sample materials that satisfied the asserted patents, but only by making substitutions that the prior art "does not teach or suggest." *Id.* at 393. Accordingly, the Court held that anticipation through inherency had not been proven by the experiments. *Id.*

The present case is in contrast to *Wesley Jessen*. Unlike that case, the Proudfit combination balls were taught in the prior art. The Molitor '751 and Wu references expressly teach to substitute polyurethane for the outer cover of a ball like Proudfit. Ex. 3, Molitor '751 at 3:9-11; Ex. 4, Wu at 1:40-43. Also, the tested balls adhered to the prior art's teachings. Thus, neither the holding nor the reasoning of *Wesley Jessen* supports Callaway's position.

Since the testing of the Proudfit combination balls show what one of ordinary skill in the art would have readily known from the teaching of the Proudfit patent and the polyurethane references, it is probative evidence of obviousness (in view of Callaway's flawed "on the ball" claim construction argument) and should be admitted.

B. The Testing of the Nesbitt Combinations is also Probative of Obviousness and Anticipation

The testing of the Nesbitt combination balls⁸ is also relevant and admissible. Acushnet relies on testing of these combinations to show that the patents-in-suit would be a) obvious in

⁸ The balls made according to the Nesbitt reference, in combination with Molitor '637, Wu, and Molitor '751, are specifically identified in Dr. MacKnight's declaration as BALL_1 – BALL_6. Ex. 7, MacKnight Decl. at ¶¶ 17-22. These balls are referred to herein as the "Nesbitt combination balls" or the "Nesbitt balls."

view of Nesbitt in combination with any of the polyurethane references; and b) anticipated by Nesbitt, incorporating by reference Molitor '637.9 As with the Proudfit combinations, the testing is used to show invalidity if Callaway's flawed claim construction is adopted. If the Court agrees with Acushnet that the claims embrace Shore D measurements that are conducted according to the ASTM D-2240 standard, Acushnet will not need to rely on the testing.

For the same reasons as stated above for the Proudfit combinations, testing of the Nesbitt combination balls, as a general matter, is relevant because it shows what one of ordinary skill in the art would be able to readily ascertain from the prior art references.

Callaway makes two specific criticisms of the Nesbitt combination. First, Callaway argues that since Nesbitt does not explicitly provide a core formulation, no ball can be made that represents the Nesbitt ball. [D.I. 282, at 13]. Second, Callaway argues that the Molitor '637 patent requires that the outer cover layer be foamed, and that the Nesbitt combination balls did not have a foamed outer cover. These arguments are addressed in turn below.

1. The Core used in the Nesbitt Combination Balls is a Reasonable Representation of the Nesbitt Core

There is no specific core formula disclosed in the Nesbitt patent. Thus, Acushnet contends that one of ordinary skill in the art would test the properties of a ball described by Nesbitt by using a core that is typical of cores that were used at the time.

The core composition used in the Nesbitt combination balls was disclosed as a "conventional" core in another Sullivan patent that issued in 1996. Ex. 8, U.S. Patent No. 5,542,677, at col. 21; 15:51-16:19 (noting that the invention of that patent could be used on any "conventional" or "standard" golf ball core and then providing an example core recipe that is

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⁹ Contrary to Callaway's arguments, there is no requirement that a person of ordinary skill in the art recognize that an inherent property would be present in the prior art reference in order to anticipate. See, e.g., Boston Scientific Scimed, Inc. v. Cordis Corp., C.A. No. 03-283-SLR, 2005 U.S. Dist LEXIS 10751, at *16 (D. Del. June 3, 2005) ("[R]ecognition of an inherent limitation by a person of ordinary skill in the art before the critical date is not required to establish inherent anticipation.").

nearly identical to that used in the Nesbitt combination balls). While this is not prior art, it is indicative of the level of ordinary skill in the art in 1995, and confirms the reasonableness of the selection of core formulation that was used in the Nesbitt combination balls. Syntex (U.S.A.) LLC v. Apotex, Inc., 407 F.3d 1371, 1379 (Fed. Cir. 2005) (references published after the priority date may evidence the level of ordinary skill at the priority date).

The reasonableness of this selection for the core of the Nesbitt ball is confirmed by the patents-in-suit themselves. The '293 patent specification, for example, provides a core composition that it says was used in the Nesbitt patent: "The ball comprising inner layer formulation D and Surlyn® 9020 identifies the ball in the Nesbitt U.S. Pat. No. 4,431,193." '293 patent, col. 20:10-12. See also '293 patent, col. 18:30-34; 19:3-5. The core composition that the '293 patent sets forth is virtually identical to the core composition that was used to represent the Nesbitt combination balls. '293 patent, col. 16:15-30.

That the choice of core recipe for the Nesbitt combination balls is consistent with how Mr. Sullivan himself described the Nesbitt prior art ball is evidence that the choice was reasonable. Since Callaway's patents-in-suit describe the Nesbitt ball as having the same core that was used in the ball testing, Callaway should not be heard to complain that the core of the tested balls is not representative of the Nesbitt patent.

Moreover, Callaway has offered no evidence that the specific choice of core has any material effect on the outer cover Shore D hardness of a golf ball. 10 Indeed, the '293 patent seems to indicate that Shore D hardness measurements of an outer cover layer whose thickness is 0.055 inches do not vary based on what materials are underneath the outer cover material. Specifically, Table 7, which according to Callaway shows "on the ball" Shore D measurements of the outer cover layer, demonstrates that the same measurement was made for each cover layer

¹⁰ This is especially important since some of the measurements for the tested balls were greatly under 64 Shore D. For example, the Nesbitt/Molitor '751 balls had an average "on the ball" Shore D hardness measurement of 49.6, and the Nesbitt/Wu balls had an average measurement of 55.6. Ex. 7, MacKnight Decl. ¶ 33. Callaway offers no evidence that a different core recipe would somehow cause these measurements to jump all the way to 64.

material, regardless of what inner cover layer or core was used. '293 patent, Table 7. Thus, there is no reason to believe that the choice of core to represent the Nesbitt combinations would have any effect on the measurements of the outer cover layer.

Callaway also does not assert that the particular core chosen for the Nesbitt combination balls skews the results or renders the Nesbitt combination ball testing not probative. Even if Callaway had any argument that the choice of core materially affected the outer cover Shore D hardness measurements of the tested balls, which Callaway does not, such an argument would go only to the weight of the Nesbitt combination prior art testing, not its admissibility. *Young Dental Mfg. Co.*, 112 F.3d at 1146; *see also Polymer Dynamics*, 2005 U.S. Dist. LEXIS 7945, at *12 (in a non-patent context, holding that "[a]ny differences between the experiment of Dr. Johnson and the actual operation of the Bayer machinery goes to the weight of Dr. Johnson's testimony, not its admissibility").

Like the Proudfit combinations, the Nesbitt combinations are also distinguishable from the experiments considered by the court in the *Wesley Jessen* case that Callaway relies on. Whereas that case involved testing that deviated from the prior art, the Nesbitt combination balls are fully consistent with the Nesbitt patent. *Wesley Jessen*, 209 F. Supp. 2d at 392-93. Since Nesbitt describes only the use of a solid core, without specifying what kind of solid core to use, the Nesbitt combination balls were made using a typical solid core of the time period consistent with cores that would have been in the knowledge of one of ordinary skill in the art in 1995.

2. Nesbitt Does Not Require that the Compositions of Molitor '637 be Foamed When Used on the Nesbitt Ball Construction

Callaway next argues that Nesbitt and Molitor '637 teach only foamable cover layers and that therefore Acushnet has not followed the teachings of these references by constructing a ball with an "unfoamed" cover.

As an initial matter, Nesbitt does not require that the cover compositions described in Molitor '637 need to be foamed when applied to the Nesbitt ball construction. Instead, Nesbitt

states only that the "foamable compositions" of Molitor '637 can be used as one or both of the cover layers of Nesbitt's three-piece ball. Ex. 5, Nesbitt col. 3:51-61. It does not require that these compositions be actually foamed. In fact, Nesbitt explicitly contemplates using these compositions with varying degrees of foaming from "unfoamed" to "slightly foamed" to "partially foamed." *Id.* at col. 3:62-4:6 ("the outer or over layer or ply 16 *may be of unfoamed or noncellular* material") (emphasis added). Thus, Callaway's complaint that the Nesbitt balls used an outer cover that is allegedly not foamed is completely irrelevant.

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Callaway's argument that Molitor '637, read in isolation, teaches away from the use of foamed cover layers of less than 0.060 inches is also misplaced. [D.I. 282, at 13-15]. While Molitor '637 states that "functional foaming" cannot be achieved with injection molding when the cover thickness is less than 0.060 inches, the Nesbitt patent explicitly says that the level of foaming can be varied for the outer cover layer, using the materials of Molitor '637, including the possibility of having an "unfoamed" outer cover layer. Ex. 5, Nesbitt col. 3:62-4:6. Thus, the cover materials of Molitor '637 can be used as the outer cover layer of the Nesbitt ball without foaming, and the suggestion of Molitor '637 to use a cover thickness of 0.060 inches or more would not be applicable to such a ball. Nesbitt explicitly teaches an outer cover layer of 0.0575 inches, and explicitly teaches that the materials of Molitor '637 can be used in that outer cover layer. *Id.* at col. 3:39-44; 3:51-61. Hence, testing of a ball with that construction is probative of what properties a ball made according to the teaching of Nesbitt, incorporating Molitor '637, would have.

Finally, even if Callaway were right that the outer cover layer of Molitor '637 must be foamed, its argument is misplaced. There is no dispute that foaming a cover layer results in an *even softer* cover layer. Ex. 9, MacKnight Tr. at 69:14-18; Ex. 10, Nesbitt Tr. at 161:10-19; Ex. 5, Nesbitt col. 3:63-4:12. Thus, arguing that the cover layer of the Nesbitt combination balls is "unfoamed" is of no help to Callaway, as increased foaming would make the ball *even softer* and thus even further below the "less than 64 Shore D" required by the patents-in-suit.

Dr. MacKnight's Testimony Would be Helpful to the Jury, and C. Should be Allowed

Acushnet has established above that the testing of the Proudfit combination balls and Nesbitt combination balls is admissible. As a separate matter, the testimony of Dr. MacKnight related to that testing is also admissible.

Dr. MacKnight is indisputably a qualified expert, competent to testify as to material sciences. He is the Wilmer D. Barrett Distinguished Professor (Emeritus) in the Polymer Science and Engineering Department at the University of Massachusetts, and has been a professor there since 1965. Ex. 7, MacKnight Decl. ¶ 2. He has about 340 publications and 8 patents in the field of polymers, including ionomers and polyurethanes, which are at issue in this case. Id. Ex. A. at 2. Callaway does not dispute that Dr. MacKnight is eminently qualified to testify as to the work he did and directed in this case.

Callaway's complaints that Dr. MacKnight did not select the materials and dimensions of the golf balls he made and tested are irrelevant. [D.I. 282, at 6-7]. Acushnet is not offering Dr. MacKnight to testify whether the combinations taught by the prior art are appropriate. Instead, Dr. MacKnight is being offered to testify that the preparation and testing of the golf balls that are expressly taught be the prior art was done correctly. He used his expertise to make and test the Proudfit and Nesbitt combination balls, as identified in his report. Ex. 7, MacKnight Decl. ¶ 33.

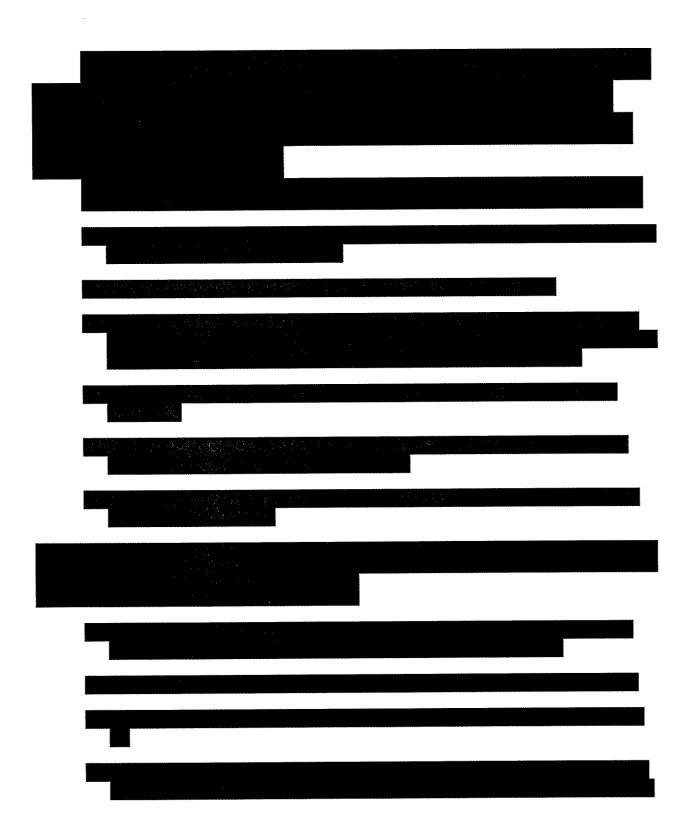
Moreover, Callaway does not, and could not, question the reliability of the methodology utilized by Dr. MacKnight to construct and test the prior art golf balls

Moreover, Spalding has utilized this technique in the past to secure patents from the PTO. See Ex. 11, CW 0323729-31.

The reliability factors set forth by the Third Circuit in Calhoun provide a useful framework for demonstrating the reliability of Dr. MacKnight's methodology (making the balls described by the prior art and measuring them):

- 2. The method has been subject to "peer review" and is "generally accepted." *Id.* Spalding utilized the same approach—measuring the Shore D values of prior art golf balls by reconstructing the balls according to the teachings of prior art references in order to get a related patent allowed. Ex. 11, CW 0323729-31.
- 3. The "known or potential rate of error" for Shore D measurements is set forth in the ASTM standard, and is not large enough to make Dr. MacKnight's results unreliable. *Calhoun*, 350 F.3d at 321.
- 4. The ASTM D-2240 sets forth "standards controlling the technique's operation." *Id.* With the exception of measuring the Shore D hardness "on the ball," as mandated by Callaway's flawed claim construction, the testing Dr. MacKnight directed conformed to the ASTM D-2240 standard. Ex. 7, MacKnight Decl. ¶ 29.
- 5. There is no question that Dr. MacKnight's qualifications are impeccable. *Calhoun*, 350 F.3d at 321.

Callaway incorrectly states that Dr. MacKnight did no more than sign off on work done by Acushnet and its lawyers. [D.I. 282, at 7]. To the contrary, Dr. MacKnight was intimately involved in supervising and approving the entire process of making and measuring the prior art golf balls.



Thus, Dr. MacKnight directed all aspects of the preparation and testing of the balls. The fact that the actual preparation and testing of the balls was by technicians at Dr. MacKnight's direction, rather than by him personally, does not affect the admissibility of his testimony. It is commonplace and appropriate for experts to rely on lab technicians to perform work at their direction. *See, e.g., In re Japanese Elec. Prods. Antitrust Litig.*, 723 F.2d 238, 277 (3d Cir. 1983) (citing C. McCormick, Evidence § 15, at 35-36 (2d ed. 1972)). The Advisory Committee Notes to Rule 703 also suggest that reliance by an expert on technicians is appropriate. Thus, Dr. MacKnight's methodology meets the reliability requirement of Rule 702.

Finally, since the prior art testing itself is relevant, as set forth above, Dr. MacKnight's testimony regarding that testing is relevant. In addition, having Dr. MacKnight testify would be helpful to the jury, since he will be in a position to explain how the materials were made and why he made the decisions he did about how to make and test the golf balls.

Had Acushnet not submitted an expert report from Dr. MacKnight, and instead just offered his testimony at trial, Callaway would have undoubtedly complained that Acushnet should have submitted an expert report. Thus, out of an abundance of caution, Acushnet timely

¹¹ PTLI is the ASTM-accredited plastics testing lab where the tests were done. Ex. 7, MacKnight Decl. ¶¶ 27-31.

submitted Dr. MacKnight's expert report setting forth the subject matter of his testimony, and Callaway took his deposition to explore the basis for the decisions he made.

Document 302

Thus, since Dr. MacKnight's methodology is reliable and his testimony is relevant, and he is qualified to offer the expertise that he does, his testimony should be admitted.

The Underlying Ball Testing Evidence is Admissible, D. Regardless of Whether Dr. MacKnight Testifies as an Expert

Acushnet has demonstrated that Dr. MacKnight's testimony is reliable and relevant, and that Dr. MacKnight is qualified to provide it. But even if the Court finds that his testimony does not contain any "opinions" that require expert testimony the underlying ball testing evidence discussed herein is nonetheless still relevant and admissible, for the reasons set forth herein. Thus, if the Court concludes that Dr. MacKnight's testimony is only a proper subject for factual testimony rather than expert testimony, Acushnet will offer Dr. MacKnight as a fact witness.

Even if Dr. MacKnight does not testify at all, Mr. Dalton and the laboratory personnel directed by Dr. MacKnight can readily testify as to how the relevant balls were made and tested. Ex. 6, Dalton Decl. ¶¶ 3-15. Callaway's improper attempt to turn its *Daubert* motion into a premature motion in limine to exclude all prior art testing evidence should be rejected.

VI. **CONCLUSION**

For the foregoing reasons, Acushnet requests that the Court deny Callaway's motion to exclude evidence of the prior art ball testing and Dr. MacKnight's testimony related thereto.

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IN THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF DELAWARE

CERTIFICATE OF SERVICE

I. Richard L. Horwitz, hereby certify that on September 27, 2007, the attached document was electronically filed with the Clerk of the Court using CM/ECF which will send notification to the registered attorney(s) of record that the document has been filed and is available for viewing and downloading.

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EXHIBIT 1

THIS EXHIBIT HAS BEEN REDACTED IN ITS ENTIRETY

EXHIBIT 2



United States Patent [19]

[54] GOLF BALL WITH IMPROVED COVER

Proudfit

5,314,187 [11] Patent Number: May 24, 1994 [45] Date of Patent:

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		Gentiluomo .		

[75]	Inventor:	James R. Proudfit, Humboldt, Tenn.
[73]	Assignee:	Wilson Sporting Goods Co., Chicago, III.

[21] Appl. No.: 905,895

[22] Filed: Jun. 29, 1992

Related U.S. Application Data

[63]	Continuation-in-part of Ser. No	o. 733,789, Jul. 26,	1991,
	abandoned.	•	

[51]	Int. Cl.5	A63B 37/12
[52]	U.S. Cl	273/235 R; 273/233;
	273/218; 27	3/228; 273/DIG. 22; 525/193;
		525/123; 525/236; 264/250
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[58] Field of Search 525/193, 123, 236; 273/235 R, 230, 218, 233

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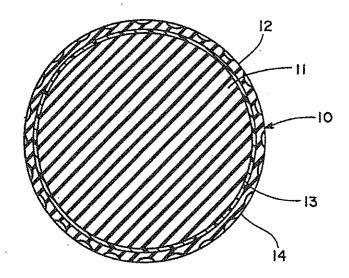
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Primary Examiner-James J. Seidleck Assistant Examiner-I. Zemel

ABSTRACT [57]

A golf ball includes a core and a cover which is formed from two separate inner and outer layers. The inner layer is molded over the core and is formed from ionomer resin. The outer layer is molded over the inner layer and is formed from a blend of natural or synthetic balata and a crosslinkable elastomer such as polybutadiene. The elastomer is thermally crosslinked with a metallic salt of an unsaturated fatty acid, such as zinc diacrylate, and a crosslinking initiator such as organic peroxide.

25 Claims, 3 Drawing Sheets



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Fig. 1

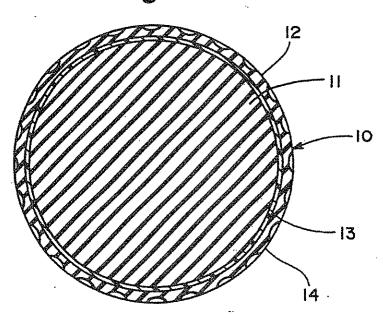
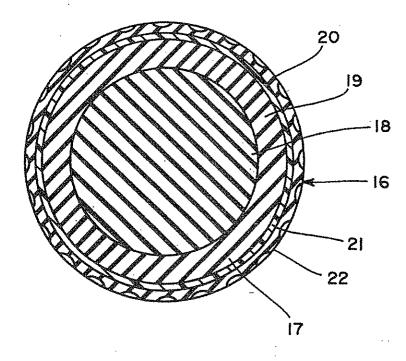


Fig. 2

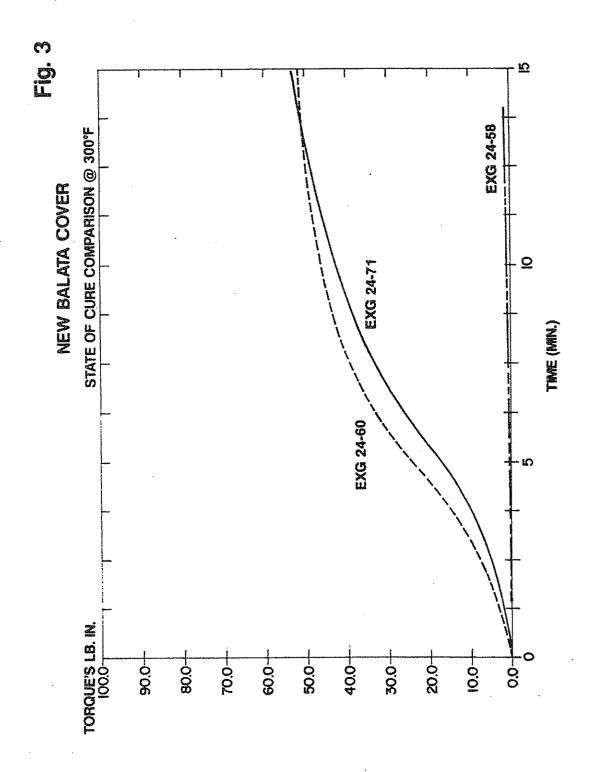


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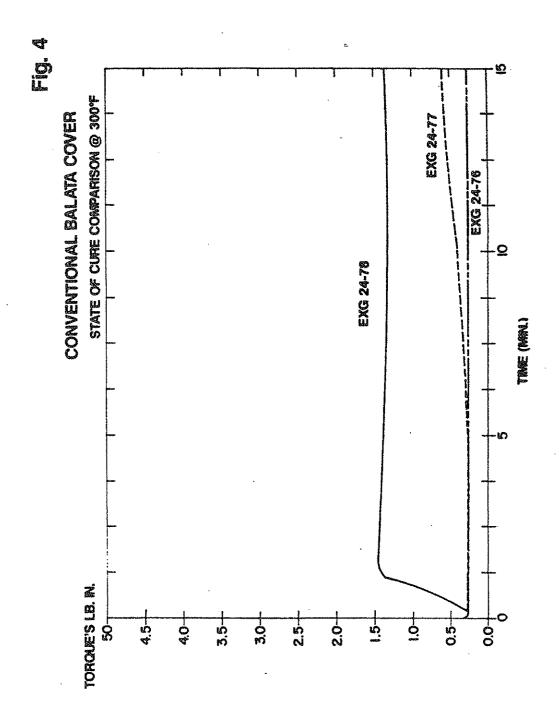


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GOLF BALL WITH IMPROVED COVER

RELATED APPLICATION

This application is a continuation-in-part application 5 of my co-pending application entitled "Golf Ball with Improved Cover," Ser. No. 733,789, filed Jul. 26, 1991, now abandoned.

BACKGROUND

This invention relates to golf balls, and, more particularly, to a golf ball having a two-layer cover. The inner layer is formed from hard resin material such as ionomer resin, and the outer layer is formed from soft material such as balata or a blend of balata and other elasto- 15

Golf balls which are currently available fall into two general categories-balls which include a balata cover and balls which include a more durable, cut-resistant cover. Balata covers are made from natural balata, syn- 20 thetic balata, or a blend of natural and synthetic balata. Natural rubber or other elastomers may also be included. Synthetic balata is trans polyisoprene and is commonly sold under the designation TP-301 available from Kuraray Isoprene Company Ltd.

Most cut-resistant covers utilize Surlyn ionomers, which are ionic copolymers available from E. I. du Pont de Nemours & Co. Suriyn ionomers are copolymers of olefin, typically ethylene, and an alpha-beta ethyleniacid. Neutralization of a number of the acid groups is effected with metal ions, such as sodium, zinc, lithium, and magnesium. DuPont's U.S. Pat. No. 3,264,272 describes procedures for manufacturing ionic copolymers. U.S. Pat. No. 3,264,272 may have a flexural modulus of from about 14,000 to about 100,000 psi as measured in accordance with ASTM method D-790. DuPont's U.S. Pat. No. 4,690,981 describes ionic copolymers which include a softening comonomer. Ionic copolymers pro- 40 duced in accordance with U.S. Pat. No. 4,690,981 are considered "soft" ionic copolymers and have a flexural modulus of about 2800 to about 8500 psi.

Other cut-resistant materials which can be used in golf ball covers are ionic copolymers available from 45 Exxon under the name lotek, which are similar to Surlyn ionic copolymers except that acrylic acid is used rather than methacrylic acid.

A number of golfers, primarily professional and low handicap golfers, prefer balata covered balls because of 50 the higher spin rate, control, "feel," and "click" which balata provides. "Feel" is the overall sensation imparted to a golfer when the ball is hit, and "click" refers to the sound made when the clubhead hits the ball. However, balata covered balls are more expensive and are less 55 9. compression mold balata balls Note: cover is only resistant to cutting than Surly covered balls.

Conventional balata covered 3 piece golf balls are produced by winding resilient, low heat-resistant elastic thread over a soft rubber or liquid rubber center, which must first be frozen to permit winding the rubber 60 13. seam buff ball being careful not to buff seam too thread, and molding a conventional soft balata cover over the windings. The balata is conventionally vulcanized or crosslinked by using sulfur as the crosslinker or vulcanizing agent.

This process has proven to be very costly and re- 65 16. remove balls from solution and water rinse quires numerous extra production steps in manufacture, extended cure time frames in hot room areas, and specified ambient conditions in order to complete the sulfur

crosslinking system. The procedures limit the consistency of the crosslinking, reduce the ability to initiate good work-in-process production procedures and maintain normal inventory levels, and limit the time frame after ball finishing for final cover crosslinking which develops the final physical properties of the cover and the ball.

In addition, conventional processing methods for balata covered balls produce relatively low yields of good cosmetic quality balls because the additional processing steps which are required before complete cover crosslinking occurs can damage the cover surface. Also, extra steps are required in conventional balata ball production methods including chlorination and ball rinses to prepare the cover surface for acceptable paint adhesion to the balata surface. Multiple coats of pigmented paint are normally applied prior to logo stamping, then a final clear, two component or ultra violet curable coating is applied to protect the ball surface and logo.

While the ball is played, additional paint durability problems may be exhibited in the form of scuffing and micro cracking. Balata golf balls produced using the conventional process methods also suffer from color 25 and color stability problems.

Surlyn covered balls are cheaper than balata balls not only because Surlyn is cheaper than balata but because the Surlyn balls can be processed after molding much easier and faster than balata balls. The substantial procally unsaturated carboxylic acid, such as methacrylic 30 cessing differences between balata balls and Surlyn balls can be see by comparing Tables 1 and 2, which describe the conventional processing steps for manufacturing 3 piece balata and 3 piece Surlyn golf balls. The term "3 piece" is commonly used to refer to a golf ball which Ionic copolymers manufactured in accordance with 35 has a center, a layer of elastic windings over the center, and a cover. The term "2 piece" is used to refer to a golf ball which has a solid core and a cover. Table 3 describes the conventional processing steps for a 2 piece Surlyn golf ball. The processing steps described in Tables 1-3 are well known in the golf ball industry, and a detailed description thereof is unnecessary.

TABLE 1

Conventional 3 Piece Balata Process

- 1. center rubber compound mixed
- 2. mill and preform pellets
- 3. mold center
- center flash removed
- 5. freeze center
- 6. wind core (conventional elastic thread)
- 7. compression mold heated preform pellets into single halfshells
- 8. place halfshells over wound core
- partially crosslinked after this molding step.
- 10. freeze molded ball prior to buffing
- 11. remove balls and transfer to fiberglass bags
- 12. transport frozen balls to holding freezer
- deep because of the soft cover
- 14. grade balls after seam buff for quality level
- 15. cure balata ball cover in alcohol/RR2 crystals solution, (7 hours soak)
- 17. transport balls into hot room to cure for 7 days
- 18. before removing balls from room use benzene test method to insure proper cover cure

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19, remove balls from cure room and soak in acetone, (hazard solvent disposal necessary)

20. remove balls from acetone and allow to air dry 21. chlorination process using hydrochloric acid and sodium hypochlorite; load balls into solution tank 5 (must be done in an exhausted area for safety), (chlo-

rination solution must be neutralized before discharge into city sewer drain)

22. remove balls and rinse in clear water tank, up and down motion

23. remove and repeat in second tank

24. remove and repeat in third tank

25. remove and rinse in acetone tank

26. apply primer

27. apply 1st top coat

28. pad print logo

29. apply clear top coat

30. inspect and package

TABLE 2

Conventional 3 Piece Surlyn Process

- 1. center rubber compound mixed
- 2. mill and preform slug
- 3, mold center
- 4. center flash removed
- 5. wind center (conventional elastic thread)
- 6. injection mold halfshells
- 7. place halfshells over core
- 8. compression mold ball
- 9. seam buff parting line
- 10. vibratory finish ball
- 11. apply primer
- 12. pad print logo
- 13. apply clear top coat
- 14. inspect and package

TABLE 3

Conventional 2 Piece Surlyn Process

- 1. core rubber compound mixed
- 2. mill and preform slug
- 3. mold core
- 4. centerless grind core to size
- 5. injection mold Surlyn cover around core
- 6. seam buff parting line
- 7. vibratory finish ball
- 8. apply primer
- 9. pad print logo
- 10. apply clear top coat
- 11. inspect and package

The balata cover is not fully cured and crosslinked 50 until the 7 day cure step of step No. 17 in Table 1 is completed. As a result, the partially cured balata balls require more careful handling and additional process steps than the Surlyn balls. For example, after the balata balls are removed from the mold they must be frozen 55 before the parting line seam on each ball is buffed. Also, because the balata covers are softer, they must be examined more carefully for defects which could be caused by the processing steps.

DESCRIPTION OF PRIOR ART GOLF BALL **CURING SYSTEMS**

As stated previously, balata covers are generally vulcanized or cured using sulfur as the vulcanizing agent. Sulfur is included in the cover composition in an 65 amount of about 1 to 2% by weight of the balata. The vulcanizing occurs during the final molding operation in which two hemispherical halfshells of the cover are

molded over the thread-wound core in a compression mold. However, the molding temperature and time is limited by the threads, which can be damaged by high heat. Accordingly, the cover is not fully cured when it is removed from the mold and requires the exposure as described in Table 1, step 15 to accelerate the cure through migration of the RR2 crystals accelerator material into the cover cross sectional area to complete the vulcanization of the cover. RR2 crystals are the reaction product of 1,1 methylene dipiperdine and carbon disulfide and are available from Rockland React-Rite. Inc. of Rockmart, Ga. RR2 crystals are dissolved in isopropyl alcohol solvent in the amount of about 10% by weight of crystals to about 90% by weight of alco-

By way of example, one specific commercial balata covered ball which was sold by Wilson Sporting Goods Co. had the cover composition described in Table 4.

TABLE 4

	Prior Art Balata Cover Com (Parts by Weight)	position
-	Trans Polyisoprene	84.00
	Natural Rubber or Polyisoprene	16.00
25	ZnO	13.00
	TiO ₂	17.00
	Blue Toner	0.20
	Stearic Acid	0.26
	Thiozole Accelerator	0.26
	Sulfur	1.20
30	Total	131.92

This system was not completely crosslinked until steps 15 through 17 were performed in Table 1.

The Zinc Oxide was used as a filler and a gravity adjuster. The blue toner was used to enhance the white color and was Ultramarine Blue from Whittaker, Clark & Daniels, Inc. of South Plainfield, N.J.

Two piece or solid golf balls conventionally include a 40 core which includes a thermally crosslinkable elastomer such as polybutadiene. The polybutadiene is cured or crosslinked by including in the core composition a crosslinking agent and a crosslinking initiator. Common crosslinking agents are zinc salts of monocarboxylic acids such as zinc diacrylate, zinc acrylate, and zinc methacrylate. The crosslinking initiator provides free radicals, and common crosslinking initiators are organic peroxides such as dicumyl peroxide.

U.S. Pat. Nos. 3,784,209, 4,065,537, 4,266,772, 4,483,537, 4,683,257, 4,688,801, 4,714,253, and 4,715,607 describe various solid cores for golf balls which include elastomers such as polybutadiene which are cured or crosslinked by zinc diacrylate and peroxide or similar ingredients.

U.S. Pat. Nos. 4,792,141 and 4,931,376 describe golf ball covers which include blends of balata and elastomers such as polybutadiene and trans polyoctenylene rubber. However, the rubber compositions are cured by 60 the conventional sulfur curing technique.

U.S. Pat. No. 4,884,814 describes a golf ball cover which is formed from a blend of "hard Surlyn" and "soft Surlyn". The hard Surlyn is described as a high modulus ionomer having a flexural modulus of from about 30,000 to 55,000 psi as measured in accordance with A.S.T.M. Method D-790. The soft Surlyn is described as a low modulus ionomer having a flexural modulus of from about 3,000 to about 7,000 psi.

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U.S. Pat. No. 4,431,193 describes a golf ball with a two-layer cover. The inner layer is formed from a hard ionomer resin having a high flexural modulus, and the outer layer is formed from a soft ionomer resin having a low flexural modulus.

SUMMARY OF THE INVENTION

The invention provides a golf ball which has many of the desirable features of balata covered balls but is more durable, more cut-resistant, and easier and less expen- 10 dium), 4000 (zinc), and 4010 (zinc.) sive to manufacture than conventional balata covered

A golf ball cover in accordance with the invention includes an inner layer formed from a relatively hard, cut-resistant material such as ionomer resin and an outer 15 layer of soft material such as balata or a blend of balata and other elastomers. Preferably, the outer layer is a blend of balata and a thermally crosslinkable elastomer such as polybutadiene. The balata and elastomer are linker such as zinc diacrylate and a crosslinking initiator such as organic peroxide rather than using the conventional sulfur and RR2 crystals curing system for balata covers. The outer layer of the cover is completely and subsequent processing steps can be performed in the same manner as on Surlyn covered balls. The inner layer of the cover provides good cut resistance, and the outer layer provides the sound, feel, and spin character-2 piece or 3 piece balls.

DESCRIPTION OF THE DRAWING

FIG. 1 is a cross section of a two piece ball formed in accordance with the invention;

FIG. 2 is a cross section of a three piece ball formed in accordance with the invention; and

FIGS. 3 and 4 are rheology charts showing curing comparisons of various balata covers.

DESCRIPTION OF SPECIFIC EMBODIMENTS OF THE INVENTION

The cover of the invention is formed from two layers -an inner layer which is molded over a solid or a wound core and an outer layer which is molded over 45 the inner layer. The inner layer is formed from a relatively hard, cut-resistant material such as ionomer resin, and the outer layer is formed from relatively soft material such as elastomeric or polymeric material selected from the class consisting of natural balata, synthetic 50 balata, natural rubber, polybutadiene, and polyoctenylene rubber. Polyoctenylene rubber having a high trans content is available under the trade name Vestenamer from Huls Corp. of West Germany. Particular grades of and Vestenamer 6213.

The ionomers used for the inner layer are available from E. I. du Pont de Nemours & Co. under the name Surlyn and from Exxon under the name Iotek. Surlyn resins are described in U.S. Pat. No. 3,264,272. As de- 60 scribed in that patent, various metal ions can be used to neutralize the acid groups, including sodium, zinc, lithium, and magnesium. The ionomer resins generally fall into three categories which are characterized by hardness or stiffness-standard, high modulus, and low mod- 65 ulus. The standard resins have a flexural modulus in the range of about 30,000 to about 55,000 psi as measured by ASTM Method D-790. (Standard resins are referred to

as "hard Surlyns" in U.S. Pat. No. 4,884,814.) The high modulus resins have a flexural modulus in the range of about 55,000 to about 100,000 psi. The low modulus resins have a flexural modulus in the range of about

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2800 to about 8500 psi.

Specific standard Surlyn resins which can be used in the inner layer include 8940 (sodium), 9910 (zinc), 7930 (lithium). Specific standard lotek resins which can be used include 8000 (sodium), 8020 (sodium), 8030 (so-

Low modulus ionomers are described in U.S. Pat. No. 4,690,981 and include a softening comonomer. Specific low modulus Surlyns which can be used in the inner layer include 8120 (sodium), 8320 (sodium), and 9320 (zinc).

Specific high modulus Surlyns which can be used in the inner layer include 8220 (sodium), 8240 (sodium), . 9220 (zinc), and AD-8181 (lithium).

The ionomer resins can be used alone or in blends of crosslinked during the molding of the ball by a cross- 20 two or more types of ionomers, for example, blends of sodium/zinc ionomers, sodium/lithium ionomers, zinc-/lithium ionomers, and sodium/zinc/lithium ionomers. Blends of ionomers of different stiffness can also be used, for example, blends of standard/high modulus crosslinked when the ball is removed from the mold, 25 ionomers, standard/low modulus ionomers, low/high modulus ionomers, and low/standard/high modulus ionomers.

The relatively soft elastomeric material of the outer layer has a flexural modulus in the range of about 20,000 isics of a balata cover. The cover can be used in either 30 to 25,000 psi, and in one specific embodiment had a flexural modulus of from 22,165 to 22,379 psi.

> The outer layer preferably comprises a blend of balata and one or more thermally crosslinkable elastomeric polymers. The balata can be either natural or synthetic 35 balata or a blend of both. The thermally crosslinkable elastomers can be those which have heretofore been used in core compositions of golf balls, for example, as described in U.S. Pat. Nos. 3,784,209, 4,065,37, 4,266,772, 4,483,537, 4,683,257, 4,688,801, 4,714,253, 40 and 4,715,607.

As described in those patents, suitable crosslinkable elastomers include homopolymers, copolymers or terpolymers of butadiene, isoprene or chloroprene. Preferably, the elastomer is 1,4 polybutadiene having a cis structure in a proportion of at least 40%. Most preferably the polybutadiene rubber contains at least 90% and even more preferably at least 95% of cis-1,4 bonds. If desired, natural rubbers, polyisoprene rubbers, styrene/butadiene rubbers, or the like may be blended with the polybutadiene rubber. Another suitable elastomer is polyoctenylene rubber having a high trans content.

The crosslinking agent can be one or more metalic salts of unsaturated fatty acids or monocarboxylic acids, particularly, zinc, calcium or magnesium salts of acrylic Vestenamer which are suitable are Vestenamer 8012 55 acid and methacrylic acid. Zinc diacrylate, zinc acrylate, and zinc methacrylate are particularly suitable.

Any of a number of known crosslinking initiators can be used. These initiators supply free radicals and include various organic peroxides such as dicumyl peroxide and n-Butyl-4, 4-bis (t-butylperoxy) valerate on calcium silicate, which is available from R. T. Vanderbilt, Inc. of Norwalk, Conn. under the trademark Varox 230XL. Suitable crosslinking agents and crosslinking initiators are described in the aforementioned patents which describe polybutadiene cores.

The balata is preferably present in a amount ranging from 25% to 99% of the total polymer content of the outer layer of the cover. The balance of the polymer

content, namely from 75% to 1% of the total polymer content, is preferably provided by polybutadiene having a high cis-1,4 content, but other suitable crosslinkable elastomers such as natural rubber, Vestenamer, etc. can be blended with the polybutadiene as desired.

The amount of the crosslinking agent generally ranges from 20 to 50 parts by weight of the total polymer content of the outer layer, and is preferably about 35 to 45 parts by weight.

from about \{ to 3\} parts by weight of the total polymer content of the outer layer, and preferably is about 2 to 2½ parts by weight.

Any suitable filler, for example zinc oxide, can be added to both the inner and outer layers of the cover. Zinc oxide not only acts as a filler and as a gravity adjuster but may also provide crosslinking. Other conventional ingredients may also be included, such as titanium dioxide and Ultramarine Blue.

FIG. 1 illustrates a two-piece golf ball 10 which includes a solid core 11 and a cover 12 which comprises a relatively hard inner layer 13 of one or more ionomer resins and a relatively soft outer layer 14 of polymeric material. The solid core can be formed in the conven- 25

FIG. 2 illustrates a three-piece golf ball 16 which includes a wound core 17 which comprises a center 18 and a layer 19 of windings of elastic thread. The center may be solid or a liquid filled balloon. Such wound 30 cores are also conventional. A cover 20 includes a relatively hard inner layer 21 of one or more ionomer resins as previously described and a relatively soft outer layer 22 of polymeric material as previously described.

The diameter of the core of either the two-piece or 35 the three-piece ball can be within the range of about 1,000 to 1,500 inch. The thickness of the inner layer can be within the range of about 0.0250 to 0.2875 inch to provide a total diameter of the inner layer and core within the range of about 1.550 to 1.590 inch. The thickness of the outer layer can be within the range of about 0.0450 to 0.0650 inch to provide a total ball diameter of 1.680 inch. The preferred dimensions are a core diameter of 1.500 inch, an inner layer thickness of 0.037 inch (inner layer diameter of 1.575 inch), and an outer layer 45 thickness of 0.0525 inch (total ball diameter of 1.680 inch).

EXAMPLE I

Two specific solid core compositions used with the 50 new two-layer cover had the composition described in Table 1. One core was used in a golf ball which was designated as a 90 compression ball, and the other core was used in a golf ball which was designated as a 100 compression ball.

TABLE 5

	Composition of Core (Parts by Weight)	
	90 Compression	100 Compression
Polybutadiene Rubber	95.00	95.00
Vestenamer 8012	5.00	5.00
Zinc Oxide	12.20	11.10
Zinc DiAcrylate	. 35.00	38.00
Antioxidant	0.80	0.80
Peroxide (Luperco 101 XL)	0.80	0.80
Liquid Monomer SR-35 (TMPTA)	1 5.00	5.00

	TABLE 5-continued	l
	Composition of Core (Parts by Weight)	
	90 Compression	100 Compression
Total	153.80	156.80

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The antioxidant was 2,2'-Methylenebis (4-methyl-6tertbutylphenol) which was obtained from R. T. Van-The amount of the crosslinker initiator can range 10 derbilt Co. of Norwalk, Conn. under the trade name Vanox MBPC.

> The peroxide is an organic peroxide available from Atochem North America Inc., Philadelphia, Pa.

The Liquid Monomer is Trimethylolpropane Triacrylate available from Sartomer, Westchester, Pa.

The core was processed according to the conventional steps:

- core rubber compound mixed
- 2. mill and preform slug
- 20 3. mold core
 - 4. centerless grind core to size.

The composition of the inner layer of the cover is described in Table 6.

TABLE 6

-	Composition of Inner L (Parts by Wei	
	Ionomer Type	Blend Ratio
	Sodium- Surlyn 8940	75%
3	Zinc- Surlyn 9910	25%

The inner layer can be molded in one of two methods:

- 1. Injection molded over the core in a manner which is conventionally used to injection mold ionomers over a solid core.
- 2. Injection mold halfshells, place halfshells over the core, compression mold the inner cover over the core.

After either method of molding the inner layer is completed, the surface is centerless ground to a preferred size of 1.575 inch in diameter prior to the final cover molding step.

The composition of the outer layer of the cover is described in Table 7.

TARIE 7

	1540000		
	Composition of Outer Lay (Parts by Weight)	rer	
	Trans PolyIsoprene (TP-301)	60.00	
0	Polybutadiene	48.00	
	Zinc Oxide	5.00	
	Titanium DiOxide	17.00	
	Ultramarine Blue color	.50	
	Zinc DiAcrylate	35.00	
	Peroxide (Varox 230 XL)	2.50	
5	Total	160.00	

Ultramarine Blue is a blue toner which is used to enhance the white color of the cover and is available from Whittaker, Clark & Daniels, Inc. of South Plain-60 field, N.J.

The outer layer of the cover was made by conventional mixing and molding procedures. The components of the composition are mixed on a mill such as a two roll mill to form slabs. Slabs are fed into a dicer which cubes 65 the cover compound prior to the injection molding to form generally hemispherical halfshells. The halfshells are placed about the inner layer of the ball in a compression molding machine which fuses the halfshells to each

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other and to the inner layer. The compression molding operation is carried out under a temperature of about 250° to 350° F. for about 5 to 10 minutes. The molding temperature causes the elastomer to crosslink, and it is believed that the ball is fully crosslinked when it is 5 removed from the compression mold.

The outer layer composition can also be used in a conventional injection molding machine to form an injection molded outer layer about the inner layer.

The rheology chart of FIG. 3 shows that the cross- 10 linking agent causes crosslinking of not only the polybutadiene but also of the balata and that the composition is fully crosslinked after the molding operation. The rheology chart was prepared by tests conducted on a Monsanto Moving Die Rheometer MDR 2000 available 15 from Monsanto Instruments & Equipment of Akron, Ohio. The rheometer is used to measure cure characteristics of rubber and measures the reaction torque as a function of cure time or degree of vulcanization. Curing was performed at 300° F.

FIG. 3 compares the following outer layer compositions.

EXG24-60: from Table 8

EXG24-71: same as EXG24-60 but without polybutadiene (100% TP301)

EXG24-58: same as EXG24-60 but without polybutadiene and peroxide

TARIFR

EXG24-60	
84.00	30
. 16.00	
13.00	
35.00	
17.00	
.50	
2.50	35
168.00	
	84.00 16.00 13.00 35.00 17.00 .50 2.50

EXG24-58 without peroxide exhibits very poor curing characteristics. The other two formulas have comparable curves, which indicate that the composition which includes balata and polybutadiene is just as crosslinkable as the composition which contains only balata and no polybutadiene.

FIG. 4 is a rheology chart which compares the three 45 outer layer compositions set forth in Table 9:

TABLE 9

	* * * * * * * * * * * * * * * * * * * *	-		
	EXG24-78	EXG24-77	EXG24-76	_
Trans Polyisoprene	84.00	84.00	84.00	
Natural Rubber	16.00	16.00	16.00	
ZnO	13.00	13.00	13.00	
TiO 2	17.00	17.00	17.00	
Ultramarine Blue	.20	.20	.20	
Stearic Acid	.26	,26	.26	
Thiozale Accelerator	.26	.26	.26	
Sulfur	1.20	1.20	_	
RR-2 Crystals	1.50	****		
Total	133.42	131.92	130.72	

Formula EXG24--78 is comparable to a conventional prior art balata cover which is cured by sulfur and the 60 4. centerless grind core to size step of soaking the completed ball in an alcohol/RR2 crystal solution described in Step No. 15 of Table 1. However, in order to test the composition on the MDR 2000 Rheometer the RR2 crystals were incorporated into the composition to simulate the subsequent soaking 65 7. injection mold halfshells of the outer layer of the step.

Formula EXG24-77 is the same as formula EXG24-78 but omits the RR2 crystals. Formula EXG24-76 is 10

the same as formula EXG24-78 but omits both sulfur and the RR2 crystals.

It is significant to note the difference between the cure rheology of the balata compositions illustrated in FIG. 4 and the new balata compositions cured by zinc diacrylate and peroxide illustrated in FIG. 3. The rheology physical properties for the compositions in FIG. 4 are so low compared to the compositions of FIG. 3 that the scale of FIG. 4 had to be changed from 0 to 100 torque units to 0 to 5 torque units in order to be meaningful. The cover composition of formula EXG24-60 of FIG. 3 has significantly higher torque than formula EXG24-78 of FIG. 4. Also, the rheology cure curve for formula EXG24-78 shows reversion, while the cure curve of formula EXG24-60 shows essentially a curve which is flatlined.

Because the balata-containing outer layer of the cover in accordance with the invention is fully crosslinked after the molding operation, the golf balls can be processed in a manner in which is very similar to the processing of Surlyn covered balls, thereby greatly facilitating the additional processing steps and reducing the overall cost of the balls. The processing steps for 3 piece and 2 piece balls formed in accordance with the invention are described in Tables 10 and 11, and these processing steps can be compared with the steps described in Tables 1-3.

TABLE 10

New 3 Piece Process

- 1 center rubber compound mixed
- 2. mill and preform slug
- 3. mold center
- 35 4, center flash removed
 - 5. wind center with heat resistant thread
 - 6. injection mold halfshells for the inner layer of the cover
 - 7. place the halfshells of the inner layer over the core
 - over the core
 - 9, grind inner cover surface to size if required
 - 10. injection mold the halfshells of the outer layer
 - 11. place the halfshells of the outer layer over the molded inner layer
 - 12. compression mold ball
 - 13. seam buff parting line
 - 14. vibratory finish ball
 - 15. apply primer
 - 16. logo print

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- 17. apply clear top coat
- inspect and package

TABLE 11

New 2 Piece Process

- 1. core rubber compound mixed
- 2. mill and preform slug
- 3. mold core
- 5. injection mold Surlyn inner layer of the cover around core or injection mold halfshells for the inner cover layer then compression mold halfshells around core
- 6. grind inner cover surface to size if required
- 8. place halfshells of the outer layer over the molded inner layer

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- 9. compression mold the halfshells of the outer layer over the inner layer
- 10. seam buff parting line
- 11. vibratory finish ball
- 12. apply primer
- 13. logo print
- 14. apply clear coat
- 15. audit inspect and package

Note: The outer layer of the cover can also be injection molded over the inner layer using conventional 10 injection molding technology.

Steps 5 and 10 through 25 in Table 1 have been eliminated using the new technology described in Tables 10 and 11. The 30 steps used to process balata covers in the old procedure have been replaced by 18 steps for 3 15 piece balls and 15 steps for 2 piece balls.

Balls formed in accordance with Example 1 (100 compression) were flight tested with an automatic hitting machine using a driver, a 5 iron, and a pitching wedge. The inventive balls were compared with Titleist 20 Tour 100 balata balls, which is a popular balata covered 3 piece ball. The comparative flight test data is found in Table 12.

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evaluated by relative comparison with other golf balls of known cut resistance.

The inventive balls formed in accordance with Example 1 were compared to Titleist Tour 100 balata, Spalding Tour Edition 100 (Soft Ionomer cover), and Ultra (Hard Surlyn cover), the comparative cut resistance data is found in Table 13.

TABLE 13

Ball I.D.	Cut Resistance Factor
Titleist Tour 100 balata	4.8
Spalding Tour Edition 100	6.2
Últra	7.3
Example 1 ball	7.0

The data presented illustrates that the inventive ball is dramatically improved for cut resistance over the Titleist Tour 100 balata ball, marginally better than the Tour Edition ball, and nearly parity to the hard Surlyn Ultra

While in the foregoing specification a detailed description of specific embodiments of the invention were set forth for the purpose of illustration, it will be under-

TABLE 12

4122				
	Carry	Difference	Total	Difference
HARD DRIVER- 7 Degree Launch Angle				
Titleist Tour 100 Balata	251.0	Base	268.7	Base
Example I ball	252.3	+1.3	272.2	+ 3.5
HARD DRIVER- 9 Degree Launch Angle				
Titleist Tour 100 Balata	250.5	Base	258.7	Base
Example 1 ball	254.0	+3.5	263.7	+7.6
HARD DRIVER- 11 Degree Lauch Angle		•		
Titleist Tour 100 Balata	249.6	Base	255.0	Base
Example 1 ball	255.0	∔5.3	262.6	+7.6
FIVE IRON		·		
Titleist Tour 100 Balata	166.6	Base	183.8	Base
Example I ball	167.1	+0.5	182.0	1.8
PITCHING WEDGE	*****	•		
Titleist Tour 100 Balata	102.6	Base	107.9	Base
Example 1 ball	103.0	+0.4	106.8	-1.1

The comparative flight test data inventive ball is measurably longer than the Titleist Tour 100 ball off the hard driver at 7, 9, and 11 launch angles. Also, the inventive ball has parity holding with five iron and wedge shots

Balls formed in accordance with Example 1 (100 compression) were subjected to the standard cut resistance test of Wilson Sporting Goods Co. The cut resistance test is conducted using a True Temper Driving Machine. The test club used is a pitching wedge. Six (6) balls of each type are tested and hit one time each approximately 1 inch above the centerline of the ball (random orientation) at standard clubhead velocities. The golf balls are inspected and graded as follows:

FACTOR	DESCRIPTION
10	No visible mark
9	Must search to find mark
8	Visible dent
7	Feel with fingernail- no cut
6	Fingernail inserts- cut
5	Fingernail inserts to core- core not visible
4	Core visible- core not cut
3	Core just cut
2	Core cut deep
1	Core destroyed

The factors of the six (6) golf balls of each type are averaged to obtain an overall factor. The golf balls are

stood that many of the details herein given may be varied considerably by those skilled in the art without 45 departing from the spirit and scope of the invention.

I claim:

- 1. A golf ball comprising a core and a cover, the cover comprising an inner layer molded over the core and an outer layer molded over the inner layer, the inner layer comprising ionomer resin and the outer layer containing natural or synthetic balata as a principal ingredient.
- The golf ball of claim 1 in which the outer layer includes a blend of natural or synthetic balata and polybutadiene.
- 3. The golf ball of claim 1 in which the outer layer includes natural or synthetic balata in an amount ranging from 25 to 99% of the total weight of polymer of the outer layer and a crosslinkable elastomer in an amount ranging form 1 to 75% of the total weight of polymer of the outer layer, said elastomer being selected from the group consisting of polyoctenylene; homopolymers, copolymers, or terpolymers of butadiene; and homopolymers, copolymers, or terpolymers of chloroprene.
 - 4. The golf ball of claim 1 in which the diameter of the core is within the range of about 1.000 to 1.500 inch, the thickness of the inner layer is within the range of about 0.0250 to 0.2875 inch, the thickness of the outer

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layer is within the range of about 0.0450 to 0.650 inch, and the diameter of the golf ball is at least 1.680 inches.

- 5. The golf ball of claim 1 in which the diameter of the core is about 1.500 inch, the thickness of the inner layer is about 0.0375 inch, the thickness of the outer 5 layer is about 0.0525 inch, and the diameter of the golf ball is 1.680 inches.
- 6. A golf bal comprising a core and a cover, the cover comprising an inner layer of ionomer resin molded over 10 the core and an outer layer molded over the inner layer, the outer layer being formed from a composition comprising:
 - a) natural or synthetic balata;
 - b) an elastomer which is crosslinkable with a metallic 15 salt of an unsaturated fatty acid, said elastomer being selected from the group consisting of polyoctenylene; homopolymers, copolymers, or terpolymers of butadiene; and homopolymers, copolymers or terpolymers of chloroprene;
 - c) a metallic salt of an unsaturated fatty acid as a crosslinking agent; and
 - d) a crosslinking initiator which provides a source of free radicals.
- 7. The golf ball of claim 6 in which the elastomer of 25 the outer layer is selected from the group consisting of polybutadiene and polyoctenylene.
- 8. The golf ball of claim 6 in which the natural or amount ranging from 25 to 99% of the total weight of 30 layer is about 0.0375 inch, the thickness of the outer polymer of the outer layer and the crosslinkable elastomer is present in an amount ranging from 1 to 75% of the total rate of polymer of the outer layer.
- 9. The golf ball of claim 6 in which the crosslinking 35 agent of the outer layer is selected from the group of zinc salts, calcium salts, and magnesium salts of monocarboxylic acids.
- 10. The golf ball of claim 6 in which the crosslinking initiator of the outer layer is organic peroxide.
- 11. The golf ball of claim 6 in which the core is a solid core.
- 12. The golf ball of claim 7 in which the core is a 2 piece core comprising a center and a layer of elastic windings over the center.
- 13. The golf ball of claim 6 in which the crosslinkable elastomer of the outer layer is polybutadiene.
- 14. The golf ball of claim 13 in which the polybutadiene is cis 1,4 polybutadiene having a cis content of at least 40%.
- 15. The golf ball of claim 6 in which the diameter of the core is within the range of about 1.000 to 1.500 inch, the thickness of the inner layer is within the range of about 0.0250 to 0.2875 inch, the thickness of the outer 55 layer is within the range of about 0.0450 to 0.650 inch, and the diameter of the golf ball is at least 1.680 inches.
- 16. The golf ball of claim 6 in which the diameter of the core is about 1.500 inch, the thickness of the inner layer is about 0.0375 inch, the thickness of the outer 60 layer is about 0.0525 inch, and the diameter of the golf ball is 1.680 inches.
- 17. A golf ball comprising a core and a cover, the cover comprising an inner layer of ionomer resin molded over the core and an outer layer molded over 65

14 the inner layer, the outer layer being formed from a composition comprising:

- a) from 25 to 99 parts by weight of natural or synthetic balata:
- b) from 1 to 75 parts by weight of an elastomer which is crosslinkable with a metallic salt of an unsaturated fatty, acid, said elastomer being selected from the group consisting of polyoctenylene, homopolymers, copolymers, or terpolymers of butadiene; and homopolymers, copolymers, or terpolymers of chloroprene;
- c) from 20 to 50 parts by weight of a metallic salt of an unsaturated fatty acid as a crosslinking agent; and
- d) from { to 3} parts by weight of a crosslinking initiator which provides a source of free radicals.
- 18. The golf ball of claim 17 in which the crosslinkable elastomer of the outer layer, is polybutadiene.
- 19. The golf ball of claim 18 in which the polybutadi-20 ene is cis 1,4 polybutadiene having a cis content of at least 40%.
 - 20. The golf ball of claim 17 in which the diameter of the core is within the range of about 1.000 to 1.500 inch, the thickness of the inner layer is within the range of about 0.0250 to 0.2875 inch, the thickness of the outer layer is within the range of about 0.0450 to 0.650 inch, and the diameter of the golf ball is at least 1.680 inches.
 - 21. The golf ball of claim 17 in which the diameter of the core is about 1.500 inch, the thickness of the inner ball is 1.680 inches.
 - 22. A method of making a golf ball comprising the steps of:
 - a) forming a spherical core;
 - b) molding ionomer resin over the core to form a first cover layer;
 - c) forming a blended composition of balata, crosslinkable elastomer, a metallic salt of an unsaturated fatty acid as a crosslinking agent, and a crosslinking initiator which provides a source of free radicals, said crosslinkable elastomer being selected from the group consisting of polyoctenylene, homopolymers, copolymers, or terpolymers of butadiene; and homopolymers, copolymers, and terpolymers of chloroprene; and
 - d) molding said blended composition over the first cover layer to form a second cover layer and to crosslink the crosslinkable elastomer.
 - 23. The golf ball obtained by the method of claim 22 in which the molding of the blended composition is performed under a temperature of about 250° to 350° F. for about 5 to 10 minutes.
 - 24. The golf ball obtained by the method of claim 22 which the diameter of the core is within the range of about 1.000 to 1.500 inch, the first cover layer is molded to a thickness within the range of about 0.0250 to 0.2875 inch, and the second cover layer is molded to a thickness within the range of about 0.0450 to 0.650 inch.
 - 25. The golf ball of claim 24 in which the diameter of the core is about 1.500 inch, the first cover layer is molded to a thickness of about 0.0375 inch, and the second cover layer is molded to a thickness of about 0.0525 inch.

EXHIBIT 3

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United States Patent [19] 4,674,751 Patent Number: [11] Molitor et al. Date of Patent: Jun. 23, 1987 [54] GOLF BALL HAVING IMPROVED 4,234,184 11/1980 Deleens et al. 273/235 R PLAYABILITY PROPERTIES 4,248,432 2/1981 Hewitt et al. 273/235 R [75] Inventors: Robert P. Molitor, Niles, Mich.; 4,295,652 10/1981 Saito et al. 273/235 R Terence Melvin, Sommers, Conn.; 4,323,247 4/1982 Keches et al. 273/235 R John L. Nealon, Springfield; David 4,337,946 7/1982 Saito et al. 273/225 4,337,947 7/1982 Saito et al. 273/235 R W. Dreifus, Longmeadow, both of 4,398,000 8/1983 Kataoka et al. 525/437 4,423,185 12/1983 Matsumoto et al. 585/312 Spalding & Evenflo Companies, Inc., [73] Assignee: FOREIGN PATENT DOCUMENTS Chicopee, Mass. 1087566 10/1967 United Kingdom . [21] Appl. No.: 858,958 1163662 9/1969 United Kingdom . [22] Filed: May 2, 1986 1210698 10/1970 United Kingdom . 1209032 10/1970 United Kingdom . 1345151 1/1974 United Kingdom . Related U.S. Application Data 1383422 2/1975 United Kingdom . - Continuation-in-part of Ser. No. 680,087, Dec. 10, Primary Examiner-Lewis T. Jacobs 1984, abandoned. Assistant Examiner-A. L. Carrillo Int. Cl.⁴ A63L 37/12 Attorney, Agent, or Firm-Lahive & Cockfield 273/DIG. 22; 273/DIG. 24; 525/127; 525/130 ABSTRACT Field of Search 525/127, 130; 273/218, Disclosed is a golf ball having improved short iron and 273/233, 234, 235 R wood playability and improved puttability relative to [56] References Cited conventional, ionomer covered balls. The golf balls comprise a novel cover which is far more durable than U.S. PATENT DOCUMENTS balata-covered balls yet closely approach or exceed 3,034,791 5/1962 Gallagher 273/235 R their playability characteristics. The cover comprises a 3,130,102 4/1964 Watson et al. 156/228 blend of a thermoplastic urethane having a Shore A 3,359,231 12/1967 Kent 524/493 Kent 427/393.5 hardness less than 95 and an ionomer having a Shore D 3,362,937 1/1968 hardness greater than 55. The relative amounts of the 3,384,612 5/1968 Brandt et al. 428/407 3,534,965 10/1970 Harrison et al. 273/218 urethane and ionomer are set so that the cover has a 3,940,146 2/1976 Little 273/235 R Shore C hardness within the range of 70 to 85, most

preferably 72 to 76.

23 Claims, No Drawings

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GOLF BALL HAVING IMPROVED PLAYABILITY **PROPERTIES**

REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 680 087 filed Dec. 10, 1984, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to golf balls and more particularly to an improved golf ball cover useful in making balls, particularly two-piece balls, having superior short iron and other playability characteristics.

Balata and blends of balata with elastomeric or plastic materials were for many years the materials of choice in the manufacture of covers for top grade golf balls These materials have good molding properties and accordingly could be readily compression molded about a 20 spherical wound core to produce a high quality golf ball. An experienced player can apply spin to a balata covered wound ball such that it will fade or draw in flight or have the backspin necessary to stop aburptly on the green. These playability properties are most 25 important in short iron play and can be exploited significantly only by relatively skilled players.

Balata and its synthetic substitutes, trans polybutadiene and trans polyisoprene, have today essentially been replaced by new materials. With the exception of a few 30 gravity, and have a desireable white color. lines of golf balls distributed through pro shops to professional golfers and those who would emulate them, newer synthetic polymers are the cover materials of choice.

used are a line of ionomers sold by E. I. Dupont de Nemours & Company under the trademark SURLYN. These materials comprise copolymers of olefins, typically ethylene, with an alpha, beta, ethylinically unsaturated carboxylic acid such as methacrylic acid. Metal ions such as sodium or zinc are used to neutralize some portion of the acidic groups in the copolymer resulting in a thermoplastic elastomer which has several advantages including a cost advantage over balata. The ionomers may be manufactured with a wide variety of properties by altering the identity of the comonomers, the fraction of the polymer comprising the carboxylic acid, the molecular weight of the polymer, the degree of neutralization of the polymer, and the identity of the 50 metal ions used. Control of these parameters results in ionomer resins of different melt index, hardness, resilience and other mechanical properties which, in a golf ball cover, affect cut resistance, shear resistance, general durability, and resilience.

U.S. Pat. No. 3,819,768 to R. P. Molitor discloses that blends of sodium neutralized ionomer resins with zinc neutralized ionomer resins, as a class, have certain advantages which have not been achievable in any other way. Among these is the production of an unexpectedly 60 high coefficient of restitution of golf balls having the blended ionomer cover. Such covers also resist cold cracking, have excellent aging properties, and are unexpectedly durable. The development of the SURLYN blended cover has been a major factor in the production 65 of two-piece balls having covers which for all practical purposes cannot be cut in play, and which travel further when hit than any other USGA regulation ball as mea-

2 sured by controlled tests when hit by golfers or testing

While the balata-covered, thread-wound balls are easily cut and very expensive, they nevertheless have excellent short iron playability. It is much more difficult to impart spin to an ionomer covered two-piece ball. Frequently, experienced players note that the ionomer covered two-piece balls have an unsatisfactory "feel".

The patent literature is replete with proposed cover 10 formulations seeking to improve upon the balata and ionomer covers which have been commercially successful. Polyurethanes, thermoplastic rubbers, various block copolymers, polyesters, and polyamides, as well as various blends including such materials, have been proposed. Examples include: U.S. Pat. Nos. 3,359,231, 4,398,000, 4,234,184, 4,295,652, 4,248,432, 3,989,568, 3,310,102, 4,337,947, 4,123,061, and 3,490,246.

The manufacture of two-piece balls i.e., balls comprising a solid, molded, resilient core and a cover, has many significant advantages over the more expensive wound balls. There is accordingly a need for two-piece balls having short iron playability characteristics comparable to wound, balata-covered balls. Such covers must have an appropriate hardness to permit the accomplished golfer to impart proper spin. In addition, it should have a resilience when formulated to have the proper hardness value consistent with a high coefficient of restitution. Also, it must be readily manufactured in large volumes at low cost, have an appropriate specific

SUMMARY OF THE INVENTION

It has now been discovered that a key to manufacturing a two-piece ball having playability properties simi-Of the new synthetics, by far the most commonly 35 lar to wound, balata-covered balls is to provide about an inner resilient molded core a cover having a shore C hardness less than 85, preferably 70-80, and most preferably 72-76. The novel cover of the golf ball of the invention is made of a composition comprising a blend of (1) a thermoplastic urethane having a shore A hardness less than 95 and (2) an ionomer having a shore D hardness greater than 55. The ionomer comprises olefinic groups having two to four carbon atoms copolymerized with acrylic or methacrylic acid groups and cross-linked with metal ions, preferably sodium or zinc ions. The primary components of the blended cover are set at a weight ratio so as to result in a cover material after molding having a shore C hardness within the range of 70 to 85, preferably 72 to 76. Preferably, the urethane component of the cover material has a tensile strength greater than 2500 psi and an elongation at break greater than 250%. A preferred cover material comprises about 8 parts of the thermoplastic urethane and between 1 and 4 parts ionomer. Preferably, the cover is no greater than 0.060 inch thick. Thinner covers appear to maximize the short iron Playability characteristics of the balls

The cover composition of the invention may be used in connection with the manufacture of thread-wound balls, but is Preferably used in the manufacture of balls having molded cores. Two-piece balls made with the cover of the invention have short iron playability properties as good as or better than balata-covered wound balls but are significantly more durable. They also have better wood playability properties than conventional two-piece balls, and permit experienced golfers to apply spin so as to fade or draw a shot. Puttability is also improved.

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Tests have shown that the spin rate off a nine iron of two-piece balls comprising the cover material of the invention is about 9,550 rpm vs. about 5,400 rpm for state of the art, two-piece balls having ionomer covers. This compares favorably to balata-covered wound balls which under the same hitting conditions have a spin rate of about 9,700 rpm. The phrase "two-piece ball" as used herein refers primarily to balls consisting of a molded core and a cover, but also includes balls having a separate solid layer beneath the cover as disclosed, for example, in U.S. Pat. No. 4,431,193 to Nesbitt, and other balls having non-wound cores.

The increased spin that can be applied during a proper hit to balls having the cover of the invention is believed to be due primarily to the softness of the 15 from the claims. blended cover material. On impact, the cover deforms significantly more than balls having ionomer covers, and tests have shown that there is a greater area of contact between the ball and the club face. This permits the better player to impart fade, draw, or backspin to 20 the ball as the situation dictates, and permits the player to execute better chips and other shots to the green. On shots of short range, e.g., less than 50 yards, the twopiece balls of the invention often outperform balatacovered wound balls. Regarding puttability, two-piece 25 balls including the cover of the invention have a lower drop rebound relative to conventional two-piece balls, and have increased contact time on the putter face. These characteristics combine to enable the player better to control the putting line and distance.

The preferred components of the cover material comprise a thermoplastic polyurethane consisting essentially of linear primary polymer chains. The structure of such chains preferably comprises long, flexible chain segments joined end to end by rigid chain segments through covalent chemical bonds. The flexible segments typically are diisocyanate-coupled, low melting polyester or polyether chains. The rigid segments include single diurethane bridges and high melting urethane chain segments formed by the reaction of diisocyanate with small glycols. Hydrogen bonding and other attractive forces among the rigid chain segments are believed to produce domains which are mutually attractive, behave somewhat like cross-links, and are reversible with heat and with solvation.

The preferred second component of the cover composition is an ionomer comprising olefinic groups having two or four carbon atoms copolymerized with acrylic or methacrylic acid groups which are at least partially neutralized with a sodium or zine ion, e.g., a 50 SURLYN ionomer. Inclusion of the ionomer imparts to the cover a degree of cut resistance far in excess of balata and helps to control the melt index of the blend to facilitate molding.

The cover composition of the invention may be used 55 to formulate golf ball covers by injection or compression molding about wound cores, solid molded cores of known composition, high coefficient molded cores such as those disclosed in copending application Ser. No. 680,088, filled Dec. 10, 1984, or cores or the type 60 claimed in copending application Ser. No. 680,085, filled Dec. 10, 1984, which has an inner, hard central portion and a soft outer layer. Various combinations of the solid core technologies may also be used.

Accordingly, it is an object of the invention to provide a cover composition which can be injection molded or compression molded about a solid molded core to produce golf ball covers which are more dura-

ble and cut resistant than balata rubber-covered balls Another object is to provide a two-piece ball having short iron and other playability characteristics equal to or exceeding thread-wound balata-covered balls Another object is to provide a cover composition compatible with urethane-based paints which resists chipping and peeling. Another object is to produce a cover for a two-piece ball which may be easily manufactured to be cut resistant and to have an improved combination of hardness and resilience properties, thereby providing a two-piece ball having both high resilience and short iron playability.

These and other objects and features of the invention will be apparent from the following description and from the claims

DESCRIPTION

The cover composition of the invention in its broadest aspects comprises a blend of a thermoplastic urethane having a shore A hardness less than 95 together with an ionomer resin having a shore D hardness greater than 55 at weight ratios sufficient to result in a golf ball cover having a shore C hardness within the range of 70 to 85, preferably within the range of 70 to 80, and most preferably 72 to 76.

The thermoplastic urethanes useful in the cover preferably consist essentially of linear primary polymer chains having a preponderence of relatively long, flexible chain segments joined end to end by rigid chain segments through covalent chemical bonds. The flexible segments may be diisocyanate coupled, low melting polyester or polyether chains. The rigid segments include single diurethane bridges resulting when a diisocyanate couples to polyester or polyether molecules. The rigid segments may comprise longer high melting urethane chain segments formed by the reaction of diisocyanate with a low molecular weight glycol chain extender component.

The polar nature of the recurring rigid, urethane chain segments results in their strong mutual attraction, aggregation, and ordering into crystalline and polycrystalline domains in the mobile polymer matrix. Urethane hydrogen atoms and carbonyl and ether oxygen partners are believed to permit extensive hydrogen bonding among the polymer chains. This apparently restricts the mobility of the urethane chain segments in the domains. These attractions and chain entanglements produce thermo-labile pseudo cross-links and produce resins which can display the superficial properties of strong rubbery vulcanizates. Preferred thermoplastic urethanes in the cover composition of the invention have a tensile strength of at least 2500 lb/in² and an elongation at break of at least 250 percent. Most preferably, tensile strength and elongation at break are 4000 lb/in2 and 400 percent, respectively.

Such materials are available commercially from Mobay Chemical Company under the trademark TEXIN, from B.F. Goodrich under the trademark ESTANE, from Upjohn Company under the trademark PELLETHANES, or from K.J. Quinn Company under the trademark Q THANES. Mobay Chemical Company's TEXIN 480AR is the currently preferred thermoplastic urethane for use in the composition of the invention, TEXIN 591A may also be used.

The other major component of the cover composition is an ionomer resin comprising a copolymer of an olefin having one to four carbon atoms with a monocarboxylic, typically acrylic or methacrylic, acid, at least 5 a r

partially neutralized with a metal ion. These materials are sold under the trademark SURLYN by E.I. Dupont de Nemours Co. and, as noted previously, come in a wide variety of grades which differ in average molecular weight, percent carboxylic acid monomer, degree of neutralization, identity of neutralizing ion, and other factors. Any of the SURLYN ionomers or other ionomers of the type described having a shore D hardness of at least 55 may be used. The currently preferred material is SURLYN 1702. SURLYN 1702 is a copolymer of ethylene and methacrylic acid which is believed to comprise about 96.5% free acid and 1.2% zinc. Its average melt index is about 14.

The presence of the ionomer in the blend serves to set 15 the melt flow index to optimal levels for injection or compression molding and also imparts cut resistence and general durability to covers made with the blend.

The urethane and ionomer resin components thus coact in use to provide a unique combination of durabil- 20 ity, playability, and ease of manufacture. The rheological properties of the blend when melted are well suited for molding covers on a commercial scale. The blend is naturally white enough so that with proper pigment additives the balls may be clear coated without painting. The nature of the cover material is such that better players can fade, draw, or apply backspin to the ball even though it is of two-piece construction, yet the cover is more cut resistant and has generally better durability than balata-covered wound balls. It is believed that the primary reason why more spin can be given to the ball during a hit is that the cover material deforms more easily than do ionomer covers. Thus, irons, particularly short irons, tend to "bite" into the 35 ball without permanently deforming it.

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The nature of the molded cores which may be used with the cover form no part of this invention, although molded cores are preferred over wound cores because of their lower cost and superior performance. Thus the 40 covers of the invention may be used with cores of the type described in U.S. Pat. Nos. 4,264,075, 4,169,599, or 4,141,559.

Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elasto- 45 mer composition comprising a high cis content polybutadiene and a metal salt of an alpha, beta, ethylinically unsaturated carboxylic acid such as zinc mono or di acrylate or methacrylate. To achieve high coefficient of restitution in the core, manufacturer include a small 50 amount of a metal oxide such as zinc oxide. Larger amounts of metal oxide than are needed to achieve coefficient may be included to increase core weight so that the finished ball more closely approaches the USGA upper weight limit of 1.620 ounce. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiator catalysts such as peroxides are admixed with the core 60 composition so that, on the application of heat and pressure, a complex curing or cross-linking reaction

Copending application Ser. No. 680,088, filed on the same day as the parent of this application, discloses a 65 golf ball core that is cured with a peroxide and a polyfunctional isocyanate. Balls having cores made using a small amount of such as isocyanate, preferably a diiso-

cyanate, e.g., 1.0%, 4.4' diphenyl methane diisocyanate, have an improved, higher coefficient of restitution. Coefficient of restitution is defined as the ratio of outgoing to incoming velocity of the test core or ball projected against a hard Plate at a selected initial velocity, e.g., 125 ft./sec. The composition may otherwise be identical to prior art polybutadiene-metal acrylate core compositions. These cores may be used with the cover composition of the invention to produce a ball of high coefficient and high initial velocity, closely approaching the USGA limit, which nevertheless has excellent short iron playability properties.

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Copending application Ser. No. 680,088, filed on the same day as the parent of this application, discloses a core consisting of a hard, inner central portion and a softer outer layer. The core may be manufactured by formulating a conventional core composition of the type described above, extruding slugs of the proper size, applying a material which alters cross-linking to surface layers of the slug, e.g., sulfur or sulfur bearing materials, and then compression molding. Inner portions of the core cure in the normal way to produce a hard, resilient center. An outer layer of the core, at least about 0.20 inches thick, is cured differently because of the presence of the sulfur or sulfur bearing material to produce a soft outer region, e.g., having a Shore A hardness of about 35. This type of core may also be used with the cover of this invention to produce balls of excellent short iron playability characteristics.

The invention will be further understood from the following non-limiting examples.

A cover composition according to the present invention was made by blending 80 parts TEXIN 480AR thermoplastic urethane (Mobay), 20 parts SURLYN 1702 (Dupont) and 0.4 parts TiO₂. After thorough blending, the cover stock had a melt flow index of 0.89. It was injection molded about conventional cores of the type described above at approximately 450 degrees F. to produce covers 0.060 in. thick. The balls were painted and their properties were tested versus a golf ball of similar construction, except that the cover material was a blend of a sodium ionomer with a zinc ionomer, and versus a wound ball having a balata cover.

Off a nine iron, balls having the cover of the invention had a spin rate of 9550 rpm, whereas ionomer covered balls had a spin rate of 5400 rpm and the balata oovered balls a spin rate of 9700 rpm. When "bladed" with a three iron, the balls of the invention are very slightly bruised, the ionomer covered balls are unmarked, and the balata covered ball is cut through to the threads. When tested by professional golfers, the balls of the invention were preceived as being equal or superior to balata covered balls for short iron playability.

A series of cover formulations were made and molded about identical one-piece cores. In these examples, the type of thermoplastic urethane and the type of ionomer used in the blend was varied, or one one of two components was eliminated, to demonstrate the effect on hardness and coefficient of the resulting golf balls. The examples also provide further teaching to those skilled in the art in the formulation of covers embodying the invention. The covers were manufactured generally as set forth in the example above using the ingredients and yielding the results set forth below.

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TABLE

\$ 1 minutes						Sample	No.	****				
	1	2	3	4	5	6	7	8	9	10	11	12
Cover												
Texin 480 AR (86 ± 3)	100	•	-	90	80	70	80	80				_
Surlyn 1702 (62)2				10	20	30			10	10	20	20
Surlyn 1706 (64) ²	_	-	*****				20	·····		_	_	
Surlyn 1605 (65) ²	`		••••		_	_	_	20	_			****
Elastollan 90 (90)1		100							90	200000	80	_
Goodrich X-4128 (93)1			100	****	_	_			-	90	****	80
Titanium dioxide	5	5	5	5	5	5	5	5	5	5	5	5
Fluorescent brightner	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Antioxidant	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Pigment	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Release agent	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Finished Ball Data												
Weight	45.2	45.3	44.9	45.1	44.7	44.5	45.0	44.8	45.1	44.8	44.4	44.5
Compression	74	70	72	72	70	73	73	70	69	71	72	74
Coefficient	.791	.788	.793	.791	.794	.787	.793	.795	.789	.790	.785	.789
Shore C Hardness	69	80	74	71	73	76	73	73	82	76 .	84	78

Shore D hardness, Elastollan 90A is a thermoplastic polyester-type arethane available commercially from BASF; Goodrich X-4128 is a thermoplastic polyester-type urethane available commercially from B. F. Goodrich.

Nos. 1, 2, and 3 are not embodiments of the invention. Sample No. 6 presented molding difficulties. Sample No. 7, 8, and 10 constitute preferred embodiments, with a Shore C hardness within the range of 72-76. Sample 4 illustrates a soft covered ball exemplifying the lower 30 range of softness in covers embodying the invention. Samples 9, 11 and 12 illustrate hard covered balls exemplifying the upper range of softness in covers embodying the invention.

It should be understood that other materials may be 35 included in the cover in addition to the essential urethane and ionomer resins discussed above, provided the cover is formulated to have the requisite Shore C hardness. For example, the hardness of a given cover embodying the invention may be adjusted slightly, and its 40 other properties may be modified by introducing into the blend compatible thermoplastic resins such as poly-

The invention may be embodied in other specific forms without departing from the spirit and scope 45 thereof Accordingly, other embodiments are within the following claims

What is claimed is:

- 1. A composition of matter for molding a cover for a golf ball, said composition comprising a thermoplastic 50 urethane polymer and said having a Shore A hardness less than 95 and an ionomer comprising olefinic groups having 2 to 4 carbon atoms copolymerized with a monocarboxylic acid having 3 to 4 carbon atoms, said acid groups being at least partially neutralized with a 55 metal ion, said ionomer having a Shore D hardness greater than 55, the relative amounts of said urethane polymer and said ionomer being sufficient to produce a cover having a Shore C hardness within the range of 70
- 2. The composition of claim 1 wherein the relative amounts of said urethane polymer and said ionomer are sufficient to produce a cover having a Shore C hardness within the range of 70 to 80.
- 3. The composition of claim 1 wherein the relative 65 amounts of said urethane polymer and said ionomer are sufficient to produce a cover having a Shore C hardness within the range of 72 to 76.

- 4. The composition of claim 1 wherein said ionomer is Cover sample number 4 is most preferred. Samples 25 neutralized with a metal selected from the group consisting of sodium and zinc.
 - 5. The composition of claim 1 comprising 8 parts of said urethane polymer and between 1 and 4 parts of said
 - 6. The composition of claim 1 further comprising titanium dioxide.
 - 7. The composition of claim 1 wherein said urethane polymer has a tensile strength of at least 2500lb/in2 and an elongation at break greater than 250 percent.
 - 8. In a golf ball having a core and a cover, the improvement wherein the cover comprises a blend of a thermoplastic urethane polymer having a Shore A hardness less than 95 and an ionomer having a Shore D hardness greater than 55, said ionomer comprising olefinic groups having 2 to 4 carbon atoms copolymerized with acrylic or methacrylic acid groups, said acid groups being at least partly neutralized with a metal ion, the relative amounts of said urethane polymer and said ionomer being sufficient to produce a cover having a Shore C hardness within the range of 70 to 85.
 - 9. The improvement of claim 8 wherein the relative amounts of said urethane polymer and said ionomer are sufficient to produce a cover having a Shore C hardness within the range of 70 to 80.
 - 10. The improvement of claim 8 wherein the relative amounts of said urethane polymer and said ionomer are sufficient to produce a cover having a Shore C hardness within the range of 72 to 76.
 - 11. The improvement of claim 8 wherein said core comprises a molded, resilient, solid sphere.
 - 12. The improvement of claim 8 wherein said ionomer is neutralized with a metal selected from the group consisting of sodium and zinc.
 - 13. The improvement of claim 8 comprising 8 parts of said urethane polymer and between 1 and 4 parts of said ionomer.
 - 14. The improvement of claim 13 comprising about 2 parts of said ionomer.
 - 15. The improvement of claim 8 wherein said cover has a thickness no greater than 0.60 inch.
 - 16. The improved golf ball of claim 8 characterized in that it has a spin rate when hit with a nine iron greater than 9,000 rpm.

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17. A golf ball cover comprising a blend of a thermoplastic urethane polymer having a Shore A hardness less than 95 and an ionomer comprising olefinic groups having 2 to 4 carbon atoms copolymerized with a monocarboxylic acid having 3 to 4 carbon atoms, said 5 acid groups being at least partially neutralized with a metal ion, said ionomer having a Shore D hardness greater than 55, the relative amounts of said urethane

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18. The cover of claim 17 wherein the relative amounts of said urethane polymer and said ionomer are sufficient to produce a cover having a Shore C hardness 15 an elongation at break greater than 250 percent. within the range of 70 to 80.

cover having a Shore C hardness within the range of 70

10 19. The cover of claim 17 wherein the relative amounts of said urethane polymer and said ionomer are sufficient to produce a cover having a Shore C hardness within the range of 72 to 76.

20. The cover of claim 17 wherein said ionomer is neutralized with a metal selected from the group consisting of sodium and zinc.

21. The cover of claim 17 comprising 8 parts of said urethane polymer and between 1 and 4 parts of said polymer and said ionomer being sufficient to produce a 10 ionomer.

22. The cover of claim 17 further comprising titanium dioxide.

23. The cover of claim 17 wherein said urethane polymer has a tensile strength of at least 2500 lb/in² and

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EXHIBIT 4



US005334673A

United States Patent [19]

Wu

[11] Patent Number:

5,334,673

[45] Date of Patent:

Aug. 2, 1994

1541	POLYURETHAN	E GOLF BALL

[75] Inventor: Shenshen Wu, North Dartmouth,

[73] Assignee: Acushnet Co., Fairhaven, Mass.

[21] Appl. No.: 814,081

[22] Filed: Dec. 24, 1991

Related U.S. Application Data

[63] Continuation of Ser. No. 556,905, Jul. 20, 1990, abandoned.

[51]	Int. Cl. ⁵
	U.S. Cl. 273/235 R; 260/998.14;
	524/874; 524/908; 524/875; 525/453
[58]	Field of Search 525/453; 524/908, 874;

260/998.41; 273/235 R

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Primary Examiner—Ralph H. Dean Attorney, Agent, or Firm—Pennie & Edmonds

[57] ABSTRACT

The golf ball is made from a composition of a polyure-thane prepolymer and a slow-reacting polyamine curing agent and/or a difunctional glycol. The slow-reacting polyamine curing agents and difunctional glycols are 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; N,N'-dialkyldiamino diphenyl methane; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 1,4-butanediol; 2,3-butanediol; 2,3-dimethyl-2,3-butanediol; ethylene glycol; and mixtures thereof.

11 Claims, No Drawings

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1 POLYURETHANE GOLF BALL

This is a continuation of application Ser. No. 07/566,905 filed Jul. 20, 1990, now abandoned.

The present invention relates to golf balls and more particularly to polyurethane covered golf balls made from a polyurethane composition of a polyurethane prepolymer cured with a slow-reacting curing agent selected from the group of slow-reacting polyamine 10 curing agents and difunctional glycols. Such a golf ball has improved resiliency and shear resistance over golf balls made from conventional polyurethane formula-

Conventionally, golf balls are made by molding a 15 cover about a core that is either a solid one-piece core or a wound core made by winding thin elastic thread about a center. The center is either a solid mass or a liquid-filled envelope which has been frozen prior to winding the thread therearound. Golf balls made from a 20 solid core are referred to conventionally as two-piece balls while those with wound cores are referred to as three-piece balls. Attempts have been made to make a one-piece golf ball, i.e. a solid homogeneous golf ball; golf ball has been made.

Balata had been used as the primary material for covers of golf balls until the 1960's when SURLYN ®, an ionomeric resin made by E.I. dupont de Nemours & Co., was introduced to the golf industry. SURLYN ® 30 costs less than balata and has a better cut resistance than balata. At the present time, SURLYN (R) is used as the primary source of cover stock for two-piece golf balls. The problem with SURLYN ®-covered golf balls, however, is that they lack the "click" and "feel" which 35 golfers had become accustomed to with balata. "Click" is the sound made when the ball is hit by a golf club while "feel" is the overall sensation imparted to the golfer when the ball is hit.

It has been proposed to employ polyurethane as a 40 cover stock for golf balls because, like SURLYN ®, it has a relatively low price compared to balata and provides superior cut resistance over balata. However, unlike SURLYN ®-covered golf balls, polyurethanecovered golf balls can be made to have the "click" and 45 "feel" of balata.

Polyurethane is the product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agent 50 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI). is either a diamine or glycol. A catalyst is often employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Conventionally, there are two categories of polyurethane on the market, thermoset and thermoplastic. 55 Thermoplastic polyurethanes are made from a diisocyanate, such as 4,4'-diphenylmethane diisocyanate (MDI) or 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), and a polyol cured with a diol, such as 1,4-butanediol. Thermoset polyurethanes are made from a diisocyanate, 60 such as 2,4-toluene diisocyanate (TDI) or methylenebis-(4-cyclohexyl isocyanate) (HMDI), and a polyol which is cured with a polyamine, such as methylenedianiline (MDA), or a trifunctional glycol, such as trimethylol propane, or tetrafunctional glycol, such as N,N,N',N'- 65 tetrakis(2-hydroxypropyl)ethylenediamine.

U.S. Pat. No. 4,123,061 issued Oct. 31, 1978 teaches that a golf ball can be made from a polyurethane pre-

polymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol or a diamine. The specific diamines taught by the '061 patent 3.3'-dichlorobenzidene; 3,3'-dichloro-4,4'ате diaminodiphenyl methane (MOCA); N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and Curalon L,

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a trade name for a mixture of aromatic diamines sold by Uniroyal, Inc. These diamines are recognized by those of skill in the art as being fast-reacting diamine curing

agents.

U.S. Pat. No. 3,989,568 issued Nov. 2, 1976 teaches a three-component system employing either one or two polyurethane prepolymers and one or two curing agents. Both polyol and diamine curing agents are taught by the '568 patent. The essential feature is that the reactants chosen for the system must have different rates of reactions within two or more competing reactions. The specific diamine curing agents taught are unhindered amines, such as methylenedianiline (MDA), and aromatic hindered amines, such as 5,5'-methylenebis-(methyl anthranilate). These diamines are recognized by those of skill in the art as being fast-reacting diamine curing agents.

It has now been discovered that a polyurethane prehowever, to date no commercially acceptable one-piece 25 polymer cured with a slow-reacting curing agent selected from the group of slow-reacting polyamine curing agents or difunctional glycols produces a golf ball cover that has good durability and performance. Golf balls made in accordance with the present invention have been found to have improved shear resistance and cut resistance compared to golf balls having covers made from either balata or SURLYN®.

Broadly, the present invention is a golf ball product made from a polyurethane prepolymer cured with a slow-reacting curing agent selected from the group of slow-reacting polyamine curing agents or difunctional glycols. The term "golf ball product" as used in the specification and claims means a cover, a core, a center or a one-piece golf ball. The cover of a golf ball made in accordance with the present invention has been found to have good shear resistance, cut resistance, durability and resiliency. Preferably, the polyurethane composition of the present invention is used to make the cover of a golf ball.

Suitable polyurethane prepolymers for use in the present invention are made from a polyol, such as polyether, polyester or polylactone, and a diisocyanate. Suitable diisocyanates for use in the present invention include 4,4'-diphenylmethane diisocyanate (MDI) and

Suitable polyether polyols include polytetramethylene ether glycol; poly(oxypropylene) glycol; and polybutadiene glycol. Suitable polyester polyols include polyethylene adipate glycol; polyethylene propylene adipate glycol; and polybutylene adipate glycol. Suitable polylactone polyols include diethylene glycol initiated caprolactone; 1,4-butanediol initiated caprolactone; trimethylol propane initiated caprolactone; and neopentyl glycol initiated caprolactone. The preferred polyols are polytetramethylene ether glycol; polyethylene adipate glycol; polybutylene adipate glycol; and diethylene glycol initiated caprolactone.

Suitable curatives for use in the present invention are selected from the slow-reacting polyamine group consisting of 3,5-dimethylthio-2,4-toluenediamine; 3,5dimethylthio-2,6-toluenediamine; N,N'-dialkyldiamino diphenyl methane; trimethylene-glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; or a difunctional glycol; and mixtures thereof. 3,5-dimethylthio-2,4-toluenediamine and 3,5-dimethylthio-2,6toluenediamine are isomers and are sold under the trade name ETHACURE ® 300 by Ethyl Corporation. Trimethylene glycol-di-p-aminobenzoate is sold under the 5 trade name POLACURE 740M and polytetramethyleneoxide-di-p-aminobenzoates are sold under the trade name POLAMINES by Polaroid Corporation. N,N'-dialkyldiamino diphenyl methane is sold under the trade name UNILINK ® by UOP.

Suitable difunctional glycols are 1,4-butanediol; 1,3butanediol; 2,3-butanediol; 2,3-dimethyl-2,3-butanediol; dipropylene glycol; and ethylene glycol. Difunctional glycols are inherently slow-reacting.

A slow-reacting curing agent with respect to amines 15 means that the amine groups on the curing agent are sterically and/or electronically hindered because of the presence of electron withdrawing groups or interfering bulky groups situated adjacent to the reaction sites. A long chain flexible spacer of at least four carbons be- 20 tween reaction sites or three carbons with electron withdrawing groups also contributes to the slower reactivity of polyamines.

Slow-reacting polyamine curing agents such as 3,5dimethylthio-2,4-toluenediamine and 3,5-dimethylthio- 25 2,6-toluenediamine are isomers with two or more of the sites on the benzene ring substituted with groups that sterically hinder the reaction ability of the amine groups. Slow-reacting polyamine curing agents such as trimethylene glycol-di-p-aminobenzoate and polytet- 30 ramethyleneoxide-di-p-aminobenzoate have the two amine groups situated adjacent to two electron withdrawing carbonyl groups,

and are separated by flexible spacers, trimethylene,

and polytetramethyleneoxide,

{(-CH2)4O]n,

respectively. Still another suitable group of polyamines comprises N,N'-dialkyldiamino diphenyl methane such as 4,4'-dibutyl diamine diphenyl methane wherein the aromatic amine group, -- \$\phi\$-NH2, is substituted by an alkyl group to become an aromatic secondary amine,

The alkyl groups attached to the amine atoms, the flexible spacers between the amine groups, electron withdrawing groups and bulky groups substituted adjacent to the amine atoms all contribute to attenuate the reac- 60 tivity of the amine, offering an increase in reaction time.

Preferably, a golf ball is made in accordance with the present invention by molding a cover about a core wherein the cover is formed from a polyurethane composition comprising a polyurethane prepolymer and a 65 mold cup made from stainless steel or brass and a core. slow-reacting polyamine curing agent or a difunctional glycol. Preferably, the cover is molded about the core in accordance with the teaching of U.S. patent applica-

tion Ser. No. 314,466 filed Feb. 22, 1989. The '466 application is incorporated herein by reference.

It has also been found that in order to alleviate the undesirable yellowish color of the polyurethane cover an effective amount of white pigment and violet agent can be added to the cover composition. Suitable violet agents include PV Fast Violet RL Special and Hostapern Violet RL Extra Strong sold by Hoechst Celanese Corporation; and Violet 23 sold by Sun Chemical Corporation. The amount of violet agent added to the cover composition is preferably about 0.0005% to about 0.002% based on total weight of cover stock. Good results have been obtained with about 0.001% by weight. Preferably, about 3.5% of white pigment by weight of the total cover composition is used in the cover stock of the present invention. Suitable white pigments include titanium dioxide, calcium carbonate, zinc oxide and zinc sulfide.

Additional components which can be added to the cover composition include U.V. stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes in conventional amounts.

There are two basic techniques used to process urethane elastomers, the prepolymer technique and the one-shot technique. The prepolymer technique requires initially the reaction between a base polyol and an excess base diisocyanate to produce a prepolymer with about 7.5% to 14% isocyanate groups (NCO). The prepolymer is further reacted with an appropriate curative to produce the elastomer. The one-shot technique utilizes the diisocyanate, the base polyol and the curative to react all in one step. The prepolymer technique is preferred because it provides better control of chemi-35 cal reaction and, consequently, results in more uniform properties for the elastomers.

The preferred process for making a molded golf ball cover in accordance with the present invention comprises an initial curing step in an open mold followed by 40 a molding step wherein the core is placed into one of the mold cups. The mold is then closed and the urethane is allowed to cure. The molding step comprises an initial molding step wherein a first mold having smoothwalled fixed-pin mold cups is used followed by a final 45 molding step wherein the smooth-surfaced golf ball product from the initial molding step is subject to a second mold having mold cups with a negative dimple pattern which is used to overmold a dimple pattern onto the smooth-surfaced golf ball product.

The preliminary curing step in the process of the present invention comprises introducing into both halves of an open mold urethane cover stock material and allowing that material to partially cure. The time necessary for the partial curing will vary, depending on 55 the exact composition of the cover stock. The applicant has found that the length of time necessary for the partial curing is about equal to the time needed for the urethane to become sufficiently adhesive between the wall of the mold cup and the core to prevent a core placed in the top mold cup from falling out of the mold cup when the top mold cup is swung over and placed on top of the bottom mold cup. Good results have been obtained at a time of about 0.5 minute. The period for the initial curing is conveniently determined between a

A convenient method for determining the length of time necessary for the initial curing step is to measure the viscosity of the urethane cover stock. Generally,

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there is about a two-fold increase in the viscosity of the polyurethane. To determine the viscosity, about 2 ml of polyurethane cover stock is placed onto a polished aluminum surface which is at an angle of 300 to the horizontal. Upon initially mixing the cover stock, pre- 5 polymer plus curing agent, the cover stock stock will travel 3 inches (7.62 cm) in about 5 seconds. At the time the initial curing step is complete, about 2 ml of the cover stock will travel 3 inches (7.62 cm) on the 30° aluminum surface in about 30 seconds.

In the initial molding step, cover stock flows about the core while pins correctly position the core inside the cover stock and a golf ball product that has substantially the size and shape of a finished golf ball is produced. While the mold can be of the retractable-pin 15 type, it is preferred to use a mold with fixed pins, i.e. pins which are not retractable. This golf ball product of the initial molding operation is subjected to a final molding step in which heat and pressure are used to impart a dimple pattern onto the smooth-surfaced golf 20 ball product and to close any pinholes which may exist.

Preferably, in the initial molding step a core, either wound or solid, is placed into the top half of a pin mold and the mold is closed and subjected to low pressure to maintain a seal between mold plates. The smooth-sur- 25 faced golf ball product of the initial molding step may be removed from the mold when the ball so produced is capable of being handled without readily becoming marred or deformed. The pins of the initial smoothwalled mold ensure proper positioning of the core dur- 30 ing this initial molding step.

In the final molding step, a compression mold is used to impart a dimple pattern upon the cover of the smooth-surfaced golf ball product. In this final molding step, the smooth-surfaced golf ball product is subjected 35 to heat and pressure such that any pinholes which are in the ball's cover are closed and such that the cover conforms to the dimple pattern of the mold halves.

It is essential that the smooth-surfaced golf ball product of the initial molding step be subjected to the final 40 molding step at a time when the cover stock is able to conform to the dimple pattern of the mold cups in the second mold. The mold used for the initial molding step may be either a fixed-pin or a retractable-pin mold. Use of a fixed-pin mold is preferable because of the lower 45 initial cost, lower operating and maintenance costs and ease of use. In either case, the size of the mold cups is about that of a conventional golf ball mold, i.e. nominally 1.68 inches (4.25 cm) for American sized balls and nominally 1.62 inches (4.10 cm) for British sized balls. 50 Both the fixed-pin and retractable-pin molds are conventional.

The mold used in the final molding step is preferably. a conventional compression mold in which each of the mold cups has a desired negative dimple pattern.

An intermediate curing step is preferably employed after the initial molding step but before the final molding step. The intermediate curing step allows the cover stock to cure to a point such that the cover stock is able to hold the dimple pattern of the mold halves of the 60 compression mold after applying the heat and pressure of the final molding step. If the intermediate curing step is too short, the cover stock is unable to retain the dimple pattern from the final molding step and a poor quality golf ball is produced. If the intermediate curing step 65 is too long, the cover stock is unable to conform to the dimple pattern of the mold halves from the compression mold. The time period for the intermediate step will

6 vary depending upon the chemical composition of the cover stock and upon the ratio of curing agent and prepolymer used in formulating the cover stock.

The length of time, temperature and pressure will vary empirically with each composition of cover stock. It has been found that the initial molding step is suitably about 5 to about 30 minutes, depending upon the mold temperature and the chemical composition of the cover stock, with enough pressure to keep the mold sealed during the initial molding step.

The intermediate curing step may also be determined empirically. It is typically up to about 1 hour at ambient temperature and pressure.

The initial molding time and the intermediate curing time can be kept to a minimum provided that a sufficient amount of the catalyst is added to the cover stock, the mold temperature is kept high, or the nature of the chemical reaction is fast.

While the length of time, temperature and pressure for the intermediate curing step may be determined empirically, it has been found that this can be calculated by using a rheometer to measure the shear resistance of the cover stock composition. The degree of cure can also be measured by a Vibrating Needle Curemeter sold by Rapra Technology Ltd.

With polyurethanes made in accordance with the present invention, the degree of cure which has taken place is dependent upon, inter alia, the time, temperature, type of curative, and amount of catalyst used. It has been found that the degree of cure of the cover composition is directly proportional to the hardness of the composition. A hardness of about 10D to 30D, Shore D hardness for the cover stock at the end of the intermediate curing step (i.e. just prior to the final molding step) has been found to be suitable for the present invention. More preferred is a hardness of about 12D to

This hardness is suitably measured with a Shore D Durometer made by Shore Instrument and Mfg. Co., Inc. The measurement is made in accordance with ASTM D 2240, "Indentation Hardness of Rubber and Plastic by Means of a Durometer." This test is performed on a 0.25-inch (6 mm) thick test plaque which has been molded for 5.5 minutes at 140° F. (60° C.) in a test slab mold. The hardness of the plaque is measured after 5.5 minutes and at one-minute intervals thereafter up to a total of 30 minutes. The length of time for the intermediate curing step can be determined when the cover stock reaches a hardness between 10D to 30D as measured by the durometer hardness measurement technique. This length of time is suitably found to be 5 to 30 minutes.

After the intermediate curing, the golf ball product is transferred to a compression mold where the final curing takes place. In this step, the golf ball product is subjected to heat and pressure to form dimples in its surface. If a fixed-pin mold was used in the initial molding step, then the final molding step closes the holes in the cover by subjecting the ball to enough heat and pressure to close the pinholes. This final curing time suitably takes about 1 to 4 minutes, with good results being obtained at about 2 minutes. The temperature is suitably about 150° F. (65.5° C.) to about 275° F. (135° C.), with good results being obtained at about 195° F. (90.5° C.) at about 1800 psi. The total final molding step, including preheating and cooling of the mold, takes approximately 8 minutes.

The dimpled golf ball product from the final molding step can be subjected to standard golf ball finishing operations such as buffing, painting, nameplating and packaging.

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These and other aspects of the present invention may 5 be further understood with reference to the following examples.

EXAMPLE 1

Thins, example illustrates making a polyurethane ¹⁰ covered two-piece golf ball in accordance with the present invention. Table I below illustrates the components used to make the golf ball cover composition:

TABLE I

		-
	Grams	
MDI prepolymer*	100.00	
Polamine 250**	48.87	
White Dispersion	5.21	

^{*}MDI prepolymer is 4.4'-diphenylmethanediisocyanate with a polyol of polytetramethylene ether glycol.

A golf ball was made having a cover formulated from the composition above following the teachings of U.S. 25 patent application Ser. No. 314,466 filed Feb. 22, 1989. This ball was tested against a conventional three-piece ball with a cover made from balata.

The golf ball of the present invention was found to be comparable as illustrated in Table II below:

TABLE II

	Present Invention	384 Tour	
PGA Compression	104	84	
Initial Velocity	252.08	252.03	
(feet/second)			
Spin Rate (rpm)			
13° (simulated driver)	2392	2600	
26" (simulated 5-iron)	4572	4721	
Distance (meters) (carry only)	222.10	220.91	•

PGA compression was measured with a PGA compression testing machine in a conventional manner. Initial velocity, spin rate and distance were measured in conventional manner. The 384 Tour is a commercial ball sold by Acushnet Company of New Bedford, Mass.

EXAMPLE 2

This example illustrates making a polyurethane covered wound golf ball in accordance with the present invention. Table III below illustrates the components used to make the golf ball cover composition:

TABLE III

117174747		
	Grams	
MDI Prepolymer*	100.00	
1,4-butanediol	11.04	
White Dispersion	3.89	
DABCO-33LV Catalyst	0.04	

The golf ball was made having a cover formulated from the composition above following the teachings of 65 U.S. patent application Ser. No. 314,466 filed Feb. 22, 1989. This ball was tested against a conventional three-piece ball with a cover made from balata.

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The golf ball of the present invention was found to be comparable as illustrated in Table IV below:

TABLE IV

		Present Invention	384 Tour
_	PGA Compression	85	85
	Initial Velocity	252.88	251.56
	(feet/second) Spin Rate (rpm)		
3	13° (simulated driver)	2753	2847
•	26" (simulated 5-iron)	4750	4672
	Distance (meters) (carry only)	219.18	218.45

It has also been found that the difunctional glycol curing agent can be used with the slow-reacting polyamine curing agent of the present invention. However, it has been found that if the slow-reacting polyamine curing agent is diluted with a difunctional glycol curing agent, the cover cuts or shears more easily than a cover made with 100% slow-reacting polyamine curing agent.

A golf ball product made in accordance with the present invention can comprise a polyurethane prepolymer cured with a curing agent system comprising 95% to 5% of a slow-reacting diamine curing agent and 5% to 95% of a diffunctional glycol curing agent. More preferably, when both curing agents are used together, about 25% to about 75% of the polyamine is used and about 75% to about 25% of the diffunctional glycol is used.

It will be understood that the claims are intended to cover all changes and modifications of the preferred embodiments of the invention herein chosen for the purpose of illustration which do not constitute a departure from the spirit and scope of the invention.

What is claimed is:

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- A golf ball comprising a core and a cover wherein said cover is made from a thermosetting polyurethane composition comprising a single polyurethane prepolymer made from any of 4,4'-diphenyl methane diisocyanate or 3,3'-dimethyl-4,4'-biphenyl diisocyanate and a polyol cured with a slow-reacting polyamine selected from the group consisting of 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine;
 N,N'-dialkyl diamino diphenyl methane; trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate and mixtures thereof.
- The golf ball of claim 1 wherein the polyol is selected from the group consisting of: polytetramethylene
 ether glycol; poly(oxypropylene) glycol; polybutadiene glycol; 1,4-butanediol initiated caprolactone diethylene glycol initiated caprolactone; trimethylol propane initiated caprolactone; neopentyl glycol initiated caprolactone; polyethylene adipate glycol; polyethylene propysene adipate glycol; and polybutylene adipate glycol.
 - 3. The golf ball of claim 1 wherein said polyurethane composition further comprises an effective amount of white pigment and violet agent to alleviate a yellow color.
 - 4. The golf ball of claim 3 wherein the amount of white pigment is about 3.5% by weight of the total polyurethane cover composition and the amount of the violet agent is about 0.0005% to about 0.002% by weight of the total polyurethane cover composition.
 - 5. A golf ball comprising a core and a cover wherein said cover is made from a single polyurethane prepolymer of a polyol, 4,4'-diphenyl methane diisocyanate and a slow-reacting curing agent, said curing agent consist-

^{**}Polamine 250 is polytetramethyleneoxide-di-p-aminobenzoate having a molecular weight of about 476 g/m.

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ing essentially of about 5% to 95% by weight of slowreacting polyamine, selected from the group consisting of 3.5-dimethylthio-2.4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; N,N'-dialkyl diamine diphenyl methane; trimethylene glycol-di-p-aminobenzo- 5 ate; polytetramethyleneoxide-di-p-aminobenzoate and mixtures thereof and about 95% to 5% by weight of difunctional glycol.

6. The golf ball of claim 5 wherein the polyol is selected from the group consisting of: polytetramethylene 10 ether glycol; poly(oxypropylene) glycol; polybutadiene glycol; 1,4-butanediol initiated caprolactone; diethylene glycol initiated caprolactone; trimethylol propane initiated caprolactone; neopentyl glycol initiated caprolactone; polyethylene adipate glycol; polyethylene propy- 15 lene adipate glycol; and polybutylene adipate glycol.

7. The golf ball of claim 5 wherein the difunctional glycol curing agent is selected from the group consisting of 1,4-butanediol; 1,3-butanediol; 2,3-butanediol; 2,3-dimethyl-2,3-butanediol; dipropylene glycol; ethyl-20 ene glycol; and mixtures thereof.

8. The golf ball of claim 5 wherein said cover further comprises an effective amount of white pigment and violet agent to alleviate a yellow color.

9. The golf ball of claim 8 wherein the amount of 25 glycol. white pigment is about 3.5% by weight of the total

polyurethane cover composition and the amount of the violet agent is about 0.0005% to about 0.002% by weight of the total polyurethane cover composition.

10. A golf ball comprising a core and a cover wherein said cover is made from a polyurethane composition consisting essentially of a single polyurethane prepolymer made from any of 4,4'-diphenyl methane diisocyanate or 3,3'-dimethyl-4,4'-biphenyl diisocyanate and a polyol cured with a slow-reacting polyamine curing agent, selected from the group consisting of 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6toluenediamine; N,N'-dialkyl diamino diphenyl methane; trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate and mixtures

11. The golf ball of claim 10 wherein the polyol is selected from the group consisting of: polytetramethylene ether glycol; poly(oxypropylene) glycol; polybutadiene glycol; 1,4-butanediol initiated caprolactone; diethylene glycol initiated caprolactone; trimethylol propane initiated caprolactone; neopentyl glycol initiated caprolactone; polyethylene adipate glycol; polyethylene propylene adipate glycol; and polybutylene adipate

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EXHIBIT 5

Primary Examiner-George J. Marlo

Uı	nited States Patent [19]		[11]	4,431,193		
Nes	bitt	[45] Feb. 14, 19		[45] F		Feb. 14, 1984
[54]	GOLF BALL AND METHOD OF MAKING SAME	Attorney, Agent, or F R. Bahr	<i>їгт</i> —Наггу О.	Ernsberger; Donald		
[75]	Inventor: R. Dennis Nesbitt, Westfield, Mass.	[57]	ABSTRACT			
[73]	Assignee: Questor Corporation, Tampa, Fla.			l and method of mak- s a solid (not thread-		
[21]	Appl. No.: 296,146	wound) resilient cer	nter or core, an	nd a multilayer cover		
[22]	Filed: Aug. 25, 1981	construction which involves a first layer or ply of molded hard, high flexural modulus resinous materia				
[51] [52]	Int. Cl. ³	on the core, and a flexural modulus res	second or cov sinous material	er layer of soft, low molded over the first The first layer is of a		
[58]	Field of Search	may be of resinous	material such	and 0.070 inches and as Type 1605 Surlyn nours and Company,		
[56]	References Cited			a thickness in a range		
	U.S. PATENT DOCUMENTS			nd may be of resinous marketed by E. I. du		
	701,741 6/1902 Kempshall	Pont de Nemours	and Company. Ilular first lay	Foamable materials ver or cellular cover		

13 Claims, 2 Drawing Figures

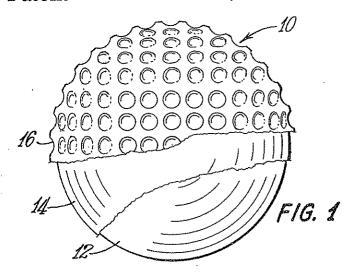
-14 LAYER OF CELLULAR OR NON-CELLULAR HARD, HIGH FLEXURAL MODULUS RESINOUS MATERIAL OF A THICKNESS IN A RANGE OF .020 AND ...

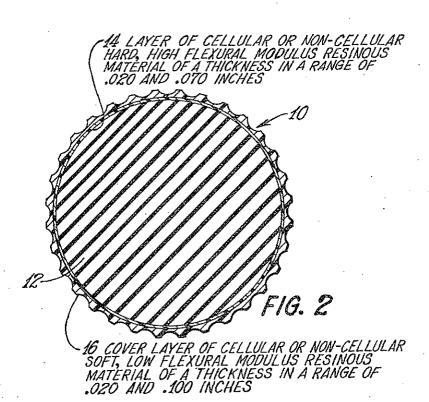
16 COVER LAYER OF CELLULAR OR NON-CELLULAR SOFT, LOW FLEXURAL MODULUS RESINOUS MATERIAL OF A THICKNESS IN A RANGE OF .020 AND .100 INCHES

U.S. Patent

Feb. 14, 1984

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GOLF BALL AND METHOD OF MAKING SAME

TECHNICAL FIELD

The invention relates to a golf ball and more particularly to a cover construction for a golf ball.

BACKGROUND ART

Golf balls having a cover material marketed under the trademark "Surlyn" by E. I. du Pont de Nemours and Company of Wilmington, Del., are known in the art and such cover compositions generally comprise a copolymer of an olefin and at least one unsaturated monocarboxylic acid. Conventional two-piece golf balls are comprised of a solid resilient center or core with molded Surlyn covers. The cover used is normally a hard, high flexural modulus Surlyn resin in order to produce a gain in the coefficient of restitution over that of the center or core.

In a conventional two-piece golf ball, a hard, high ²⁰ flexural modulus Surlyn resin is molded over a resilient center or core. The hard, highly flexural modulus Surlyn resin for the cover of a two-piece golf ball is desirable as it develops the greatest hoop stress and consequently the greatest coefficient of restitution. ²⁵

A two-piece golf ball having a hard, Surlyn resin cover however does not have the "feel" or playing characteristics associated with softer balata covered golf balls. Heretofore balata covered golf balls have been preferred by most golf professionals. If a golf ball has a cover of soft, low flexural modulus Surlyn resin moided directly over a center or core, it is found that little or no gain in coefficient of restitution is obtained.

DISCLOSURE OF THE INVENTION

In accordance with the present invention there is provided a golf ball having a multilayer or two-ply cover construction for a solid resilient center or core wherein the multilayer cover construction involves two stage molded cover compositions over a solid center or 40 core of resilient polymeric material wherein an increased coefficient of restitution is attained and wherein the "feel" or playing characteristics are attained similar to those derived from a balata covered golf ball.

The invention embraces a golf ball and method of 45 making same wherein the ball has a solid center or core of resilient polymeric or similar material covered by a first layer or ply of molded hard, highly flexural modulus resinous material or of cellular or foam composition which has a high coefficient of restitution.

The first layer or ply is provided with a second or cover layer of a comparatively soft, low flexural modulus resinous material or of cellular or foam composition molded over the first layer and core or center assembly. Such golf ball has the "feel" and playing characteristics 55 simulating those of a softer balata covered golf ball.

Through the use of the first ply or layer of hard, high flexural modulus resinous material on the core or center, a maximum coefficient of restitution may be attained. The resinous material for the first ply or layer 60 may be one type of Surlyn marketed by E. I. du Pont de Nemours and Company of Wilmington, Del., and the other ply or cover layer may be of a different type of Surlyn resin also marketed by the same company.

The three-piece golf ball of the invention provides a 65 golf ball in which the coefficient of restitution of the golf ball closely approaches or attains that which provides the maximum initial velocity permitted by the

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United States Golf Association Rules of two hundred fifty feet per second with a maximum tolerance of two percent, which velocity may be readily attained and the playing characteristics or "feel" associated with a balata covered ball secured while maintaining a total weight of the golf ball not exceeding 1.620 ounces without sacrificing any advantages of a golf ball having a standard Surlyn cover of the prior art or a golf ball having a softer balata cover.

Further objects and advantages are within the scope of this invention such as relate to the arrangement, operation and function of the related elements of the structure, to various details of construction and to combinations of parts, elements per se, and to economies of manufacture and numerous other features as will be apparent from a consideration of the specification and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The details of the invention will be described in connection with the accompanying drawings in which:

FIG. 1 is a view of a golf ball embodying the invention illustrating portions of the multiply or multilayer cover construction on a core or center, and

FIG. 2 is a diametrical cross sectional view of the golf ball of the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

Referring to the drawings in detail there is illustrated a golf ball 10 which comprises a solid center or core 12 formed as a solid body of resilient polymeric material or rubber-like material in the shape of a sphere. Disposed on the spherical center or core 12 is a first layer, lamination, ply or inner cover 14 of molded hard, highly flexural modulus resinous material such as type 1605 Surlyn marketed by E. I. du Pont de Nemours and Company, Wilmington, Del.

This material of the inner layer 14 being a hard, high flexural modulus resin produces a substantial gain of coefficient of restitution over the coefficient of restitution of the core or center. An outer layer, ply, lamination or cover 16 of comparatively soft, low flexural modulus resinous material such as type 1855 Surlyn marketed by E. I. du Pont de Nemours and Company is then re-molded onto the inner ply or layer 14, the outer surface of the outer layer or cover 16 being of dimpled configuration providing a finished three-piece golf ball.

According to the United States Golf Association Rules, the minimum diameter prescribed for a golf ball is 1.680 inches and the maximum weight prescribed for a golf ball is 1.620 ounces. It is therefore desirable to produce a golf ball having an improved coefficient of restitution to attain an initial velocity for the golf ball approaching the maximum velocity limit of 255 feet per second, the maximum limit provided by the United States Golf Association Rules.

The hard, high flexural modulus resin is employed to increase the coefficient of restitution in order to attain or approach the maximum initial velocity for the golf ball. The use of a soft low flexural modulus resin provides little or no gain in the coefficient of restitution and may tend to reduce the coefficient of restitution thereby adversely affecting the initial velocity factor.

In producing the golf ball of the invention, the density of the center or core may be varied and the relative thicknesses of the layers, plies or laminations 14 and 16

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may be varied within limits so that the golf ball weight does not exceed 1.620 ounces, the minimum diameter not less than 1.680 inches, and the ball be capable of an initial velocity approaching 255 feet per second. However, the finished golf ball may be of larger diameter 5 providing the total weight of the ball does not exceed 1.620 ounces.

Thus, by varying the density of the center or core 12 and varying the thicknesses of the plies or layers 14 and 16 of the cover construction, a golf ball may be pro- 10 duced having a total weight not exceeding 1.620 ounces and a minimum diameter of 1.680 inches and having a comparatively high coefficient of restitution, the ball closely approaching or attaining in play the maximum permitted initial velocity of 255 feet per second.

In the golf ball of the invention the thickness of the inner layer or ply 14 and the thickness of the outer layer or ply 16 may be varied to secure the advantages herein mentioned. It is found that the inner layer 14 of hard, high flexural modulus resinous material, such as Surlyn resin type 1605, is preferably of a thickness in a range of 0.020 inches and 0.070 inches. The thickness of the outer layer or cover 16 of soft, low flexural modulus resin, such as Surlyn type 1855, may be in a range of 25 0.020 inches and 0.100 inches.

For example, a center or core 12 having a 0.770 coefficient of restitution is molded with a layer of hard, high modulus Surlyn resin, such as Surlyn type 1605, to form a spherical body of a diameter of about 1.565 inches. 30 This spherical body comprising the core or center 12 and layer 14 of the hard, high modulus Surlyn resin has a coefficient of restitution of 0.800 or more.

This center or core 12 and inner layer 14 of hard resinous material in the form of a sphere is then re- 35 molded into a dimpled golf ball of a diameter of 1.680 inches minimum with an outer or cover layer 16 of a soft, low flexural modulus resin such as Surlyn type 1855. The outer layer of the soft resin is of a thickness of 0.0575 inches. The soft Surlyn resin cover would have 40 about the same thickness and shore hardness of a balata covered golf ball and would have the advantageous "feel" and playing characteristics of a balata covered golf ball.

It is to be understood that the golf ball of the inven- 45 tion may be made of a diameter greater than 1.680 inches without exceeding the total weight of 1.620 ounces by varying the thickness of the inner layer or ply 14 and the outer cover layer or ply 16 and secure desired "feel" and playing characteristics.

The inner, intermediate, or first layer or ply 14 and the outer cover, second layer or ply 16 or either of the layers may be cellular when formed of a foamed natural or synthetic polymeric material. Polymeric materials are preferably such as ionomer resins which are foam- 55 able. Reference is made to the application Ser. No. 155,658, of Robert P. Molitor issued into U.S. Pat. No. 4,274,637 which describes a number of foamable compositions of a character which may be employed for one

The inner, intermediate or first layer 14 on the core 12 may be preferably partially or only slightly foamed to a low degree so as not to materially affect the coefficient of restitution of the material. The outer or cover 65 layer or second layer 16 may be foamed to a greater degree than the inner, intermediate or first layer 14 as the material of the layer 16 is comparatively soft.

The inner, intermediate or first layer 14 may be unfoamed or noncellular and the outer layer may be cellular or foamed resin. If certain characteristics are desired for the golf ball, the inner layer 14 may be slightly or partially foamed and the outer or cover layer or ply 16 may be of unfoamed or noncellular material.

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Through the use of foamable material for the first layer, the cover layer or both layers, the degree of foaming of one or the other or both layers may be altered to provide a variation in the coefficient of restitution of the golf ball.

It is apparent that, within the scope of the invention, modifications and different arrangements may be made other than as herein disclosed, and the present disclosure is illustrative merely, the invention comprehending all variations thereof.

I claim:

- 1. A golf ball comprising a spherically-shaped solid core of resilient material, a first layer of hard, high flexural modulus ionomer resin molded onto the core, and a cover layer of soft, low flexural modulus ionomer resin molded over the first layer of ionomer resin on the core, the total weight of the golf ball not exceeding 1.620 ounces.
- 2. A golf ball comprising a spherically-shaped solid core of resilient polymeric material, a first layer of hard, high flexural modulus ionomer resin molded onto the core, and a second layer of soft, low flexural modulus ionomer resin molded over the first layer of ionomer resin on the core, the total weight of the golf ball not exceeding 1.620 ounces.
- 3. A golf ball comprising a spherically-shaped solid core of resilient polymeric material, a layer of comparatively hard, high flexural modulus ionomer resin molded onto the core, the exterior surface of the layer being of spherical configuration, and a cover layer of comparatively soft, low flexural modulus ionomer resin molded over the layer of hard, high flexural modulus ionomer resin, the outer surface of the cover layer being of dimpled configuration, the total weight of the golf ball not exceeding 1.620 ounces.
- 4. A golf ball comprising a spherically-shaped solid core of resilient material, a hard, high flexural modulus ionomer resin molded onto the core forming a layer on the core, a soft, low flexural modulus ionomer resin molded over the layer of high flexural modulus ionomer resin providing a cover layer of generally spherical shape, the exterior surface of said cover layer being of dimpled configuration, the total weight of the golf ball not exceeding 1.620 ounces, and the diameter of the golf ball being not less than 1.680 inches.
- A golf ball according to claim 4 wherein the layer of hard, high flexural modulus ionomer resin is of a thickness in a range of 0.020 inches and 0.070 inches.
- 6. A golf ball according to claim 4 wherein the cover layer of soft, low flexural modulus ionomer resin is of a thickness in a range of 0.020 inches and 0.100 inches.
- 7. A three-piece golf ball comprising a sphericallyor both layers 14 and 16 for the golf ball of this inven- 60 shaped solid core of resilient material, a comparatively hard, high flexural modulus ionomer resin molded onto the core forming a layer of the hard, high flexural modulus ionomer resin on the core, and a comparatively soft, low flexural modulus ionomer resin molded onto the layer of hard, high flexural modulus ionomer resin forming a cover layer, the exterior surface of the cover layer being a dimpled configuration and generally of spherical shape, the total weight of the golf ball not

4,431,193

exceeding 1.620 ounces, and the diameter of the golf ball being not less than 1.680 inches.

8. A three-piece golf ball comprising a sphericallyshaped solid core of resilient material, a hard, high flexural modulus surlyn resin molded onto the core 5 forming a first layer of spherical configuration on the core, a soft, low flexural modulus SURLYN resin molded over the first layer of hard, high flexural modulus SURLYN resin to form a cover layer of spherical configuration, the exterior surface of the cover layer 10 being of dimpled configuration, and the total weight of the golf ball not exceeding 1.620 ounces.

9. A golf ball comprising a spherically-shaped solid core of resilient material, a first layer of hard, high flexural modulus ionomer resin molded onto the core, 15 and a cover layer of soft, low flexural modulus foamable ionomer resin molded over the first layer of ionomer resin on the core, said cover layer being foamed to a cellular condition, the total weight of the ball not exceeding 1.620 ounces.

10. A golf ball comprising a spherically-shaped solid core of resilient material, a first layer of hard, high flexural modulus foamable ionomer resin molded onto the core, said first layer being foamed to a cellular condition, and a cover layer of soft, low flexural modulus 25 ionomer resin molded over the first layer of foamable ionomer resin on the core, the total weight of the ball not exceeding 1.620 ounces.

11. A golf ball comprising a spherically-molded solid core of resilient material, a first layer of hard, high flexural modulus foamable ionomer resin molded onto the core, said first layer being foamed to a cellular condition, and a cover layer of soft, low flexural modulus foamable ionomer resin molded over the first layer of ionomer resin, said cover layer being foamed to a cellular condition, the total weight of the ball not exceeding 1.620 onnces.

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Filed 09/27/2007

12. The method of producing a three-piece golf ball including providing a solid core of resilient material of spherical configuration, molding onto the core a hard, high flexural modulus ionomer resin providing a first layer on the core, molding a soft, low flexural modulus ionomer resin onto the first layer providing a cover layer of spherical shaped wherein the total weight of the golf ball does not exceed 1.620 ounces and the ball being of a diameter not less than 1.680 inches.

13. The method of producing a three-piece golf ball 20 including providing a solid core of resilient polymeric material of spherical configuration, molding onto the core a hard, high flexural modulus SURLYN resin providing a first layer on the core, molding a soft, low flexural modulus Surlyn resin onto the first layer providing a cover layer of spherical shape wherein the total weight of the golf ball does not exceed 1.620 ounces and the ball being of a diameter not less than 1.680 inches. * * * *

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EXHIBIT 6

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IN THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF DELAWARE

CALLAWAY GOLF COMPANY)	
Plaintiff,)	
v.)	
ACUSHNET COMPANY,)	C. A. No. 06-91 (SLR)
Defendant:	Ś	

DECLARATION OF JEFFREY L. DALTON IN SUPPORT OF ACUSHNET'S MOTION FOR SUMMARY JUDGMENT OF INVALIDITY OF U.S. PATENT NOS. 6,210,293; 6,506,130; 6,503,156; AND 6,595,873

I, Jeffrey L. Dalton, hereby state as follows:

- I am employed at the Acushnet Company ("Acushnet"), located at 333
 Bridge Street, Fairhaven, Massachusetts 02719.
 - 2) My current job title is Vice President of Intellectual Property.
- 3) I personally directed and witnessed the creation of golf ball materials and golf balls at the direction of Dr. William MacKnight, who has been retained by Acushnet in the above-captioned litigation.
- 4) I met with Dr. MacKnight in early May 2007 to discuss the preparation of golf balls materials and golf balls. Troy Lester, Acushnet's Chief Patent Counsel, was also present during that meeting. During that meeting, Dr. MacKnight and I discussed which materials and golf balls to make, and by the conclusion of the meeting, Dr. MacKnight had instructed me to make certain materials and certain golf balls with various combinations of core formulations and diameter, inner cover layer formulations and thicknesses, and outer cover formulations and thicknesses.

- 5) Specifically, Dr. MacKnight instructed me to make twelve (12) samples each of twelve (12) different constructions of golf balls. The first 9 golf ball constructions that I was instructed to make are accurately set forth in Dr. MacKnight's declaration, and are identified as BALL_1, BALL_2, BALL_3, BALL_4, BALL_5, BALL_6, BALL_7, BALL_8, and BALL_9. MacKnight Decl. ¶¶ 17-25. Dr. MacKnight's declaration is attached to his Expert Report, which is attached hereto as Exhibit A. Dr. MacKnight also instructed me to make twelve (12) samples of BALL_4, BALL_5, and BALL_6, but without the Blowing Agent Master Batch B in the inner cover layer.
- Dr. MacKnight also directed me to create seven "plaques" of cover layer materials. Six of those materials are accurately described by Dr. MacKnight in his declaration as ICL_1, ICL_2, ICL_3, OCL_1, OCL_2, and OCL_3. MacKnight Decl. ¶¶ 10-15. The seventh material was the blend described in Dr. MacKnight's report as ICL_2, but without the Blowing Agent Master Batch B. MacKnight Decl. ¶ 11.
- 7) During the meeting with Dr. MacKnight, I showed Dr. MacKnight the manufacturing equipment that would be used to create the materials and golf balls he directed, and discussed the procedures that would be used to create those materials and golf balls. Dr. MacKnight approved the process and equipment that I told him I would use.
- Subsequent to my meeting with Dr. MacKnight, I personally directed and witnessed the creation of the balls that Dr. MacKnight had directed me to make. In particular, I created twelve (12) samples each of the nine (9) different constructions that he sets forth in his declaration as BALL_1 through BALL_9. MacKnight Decl. ¶ 17-25. I also created twelve (12) samples each of BALL_4, BALL_5, and BALL_6, but without the Blowing Agent Master Batch B in the inner cover layer. I also personally directed the placement of a dimple pattern on each ball and the painting and finishing of each ball. I also personally directed and witnessed the creation of the plaques of cover layer material that I describe in paragraph 6 above. I personally inspected the balls and materials during and after their creation to ensure that they had the compositions that are described in Dr. MacKnight's expert report.

- 9) I have read and understand Dr. MacKnight's description of the balls that I made, and Dr. MacKnight's description accurately describes the balls that I made.

 MacKnight Dec. ¶¶ 7-26. If called to testify at trial I would testify that the balls that I created have the material compositions and properties that are set forth in Dr.

 MacKnight's expert report.
- 10) On or about May 17, 2007, I brought the material plaques and balls that I had made to the Plastics Testing Lab, Inc. ("PTLI") facility in Pittsfield, Massachusetts, which I understand is an accredited tester for Shore D hardness. I also brought samples of Wilson Ultra Tour Balata 90 and Wilson Ultra Tour Balata 100 balls from Acushnet's archives. Mr. Lester accompanied me. There, I met with Dr. MacKnight and James Galipeau, the Laboratory Manager.
- 11) Dr. MacKnight explained to Mr. Galipeau what tests to be performed on the golf balls we brought to PTLI. Specifically, he explained that he wanted to have the lab perform Shore D hardness measurements on the surface of the formed golf balls. Dr. MacKnight explained that he wanted the tests to be performed in accordance with ASTM D-2240, with the exception that the tests would be performed on the surface of the golf ball rather than on a plaque of material as required by ASTM D-2240.
- 12) Dr. MacKnight also directed Mr. Galipeau to perform the following measurements on the material plaques that were provided to him: a) flexural modulus tests according to ASTM D-790; b) Shore D tests according to ASTM D-2240; and c) measurements of the thickness of the plaques of materials.
- 13) Mr. Galipeau showed Dr. MacKnight and me the test equipment that was to be used for the tests, and Dr. MacKnight approved the procedures and equipment that were to be used for the measurements.
- 14) I have read and understand Dr. MacKnight's description of the testing that PTLI was instructed to perform, and Dr. MacKnight's description accurately describes what was communicated to PTLI. MacKnight Dec. ¶¶ 27-31.
- 15) On May 23, 2007, Mr. Galipeau emailed the results of PTLI's testing to Mr. Lester, who forwarded the email to me. A true and correct copy of the testing report that was sent by PTLI is attached hereto as Exhibit B.

I declare, under penalty of perjury, that the foregoing is true and correct. I would testify to the foregoing facts if called to do so in Court.

Executed on: August 24, 2007

Exhibit A To Dalton Declaration

IN THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF DELAWARE

CALLAWAY GOLF COMPANY,)
Plaintiff,) C.A. No. 06-91 (SLR)
v.)
ACUSHNET COMPANY,)
Defendant.	Ś

EXPERT REPORT OF DR. WILLIAM J. MACKNIGHT

- 1. My name is William J. MacKnight. I submit this report to describe testing I have performed related to invalidity arguments that have been made by Acushnet with respect to U.S. Patent Nos. 6,210,293 ("the '293 patent"), 6,503,156 ("the '156 patent"), 6,506,130 ("the '130 patent"), and 6,595,873 ("the '873 patent") (collectively the "Sullivan patents"). I have personal knowledge of the matters discussed herein, and I would testify to them under oath if called upon to do so.
- 2. I hold the position of Wilmer D. Barrett Distinguished Professor (Emeritus) in the Polymer Science and Engineering Department at the University of Massachusetts. I have been a professor at the University of Massachusetts since 1965, and was named Wilmer D. Barrett Distinguished Professor in 1998.
 - My educational background is summarized as follows:
 - 1958: B.S. in Chemistry (with Distinction), University of Rochester
 - 1963: M.A. in Chemistry, Princeton University
 - 1964: Ph.D. in Physical Chemistry, Princeton University
 - 1964: NSF Cooperative Fellow, Princeton University
- 4. I consider myself an expert in the field of polymer science, based on my years of teaching and research in that area. My resume is attached to this report as Exhibit A.

- 5. I understand Acushnet has presented arguments regarding the patentability of the Sullivan Patents in relation to several prior art references, including U.S. Patent No. 4,431,193 to Nesbitt ("Nesbitt 193), U.S. Patent No. 5,314,187 to Proudfit ("Proudfit 187"), U.S. Patent No. 4,274,637 to Molitor ("Molitor 637"), U.S. Patent No. 5,334,673 to Wu ("Wu 673"), and U.S. Patent No. 4,674,751 to Molitor ("Molitor 751").
- 6. I was asked by Acushnet and its lawyers to direct the preparation and testing of certain golf balls that are described by the patents listed above, or combinations thereof. 1 personally directed the preparation and testing of such golf balls.
- 7. The methods by which I prepared and tested the golf balls, and the results of those tests, are set forth in detail in the declaration I submitted to the Patent Office, which is attached to this report as Exhibit B. If asked to do so, I will testify at trial regarding the testing I performed.

Respectfully,

Dr. William J. Mecknight

Dated: June 1, 2007

EXHIBITA

WILLIAM J. MACKNIGHT

Wilmer D. Barrett Distinguished Professor Emeritus Polymer Science and Engineering Department

Education

B.S. in Chemistry (with Distinction), University of Rochester 1954-58

M.A. in Chemistry, 1963 Princeton University, 1961-64

Ph.D. in Physical Chemistry, 1964 NSF Cooperative Fellow, 1964

Post Doctoral

Research Associate in Chemistry, Princeton University (with A.V. Tobolsky) 1964-65

Military Service

U.S. Navy. Initial rank, Ensign; final rank, Lieutenant 1958-61

Employment

1965-	University of	Massachusetts
	1965-69	Assistant Professor of Chemistry
	1969-74	Associate Professor of Chemistry
	1974-76	Professor of Chemistry
	1976-85	Professor and Head, Polymer Science and Engineering
	1985-88	Professor, Polymer Science and Engineering
	1988-95	Professor and Head, Polymer Science and Engineering
	1995-96	Professor, Polymer Science and Engineering
	1996-98	Distinguished University Professor, Polymer Science and Engineering
	1998-1999	Wilmer D. Barrett Distinguished Professor
	1999-	Wilmer D. Barrett Distinguished Professor Emeritus

Some Recent Activities

Visiting Professor, Department of Chemical Engineering and Chemical Technology, Imperial College, London, England, 1979 and 1996

Member, Editorial Board, Macromolecules, 1981-84

Member, Evaluation Panel for the Center for Material Science, National Bureau of Standards, 1982-88

Member, National Academy of Sciences, National Research Council Board of the Conference on Insulation and Dielectric Phenomena, 1981-84

Chairman of the Gordon Conference on Polymers (West), 1982

Chairman of the Gordon Conference on Dielectric Phenomena, 1982

Chairman of the Gordon Conference on Ion-Containing Polymers, 1985

Member Research Briefing Panel on Polymeric Structural Materials of the National Research Council, 1984

Member, Science and Technology Advisory Council, Alcoa, 1984-86

Member, Board of Trustees, Plastics Institute of America, 1984-87

Member, Governing Board, Council of Chemical Research, 1982-85

Member, Technical Advisory Board, Diversitech General, 1984-87 Member, Council of the Gordon Research Conferences, 1984-1988 Member, Editorial Board, Polymers for Advanced Technologies, 1988-Member, Editorial Board, Acta Polymerica, 1992-Member, Editorial Board, Gels and Networks, 1992-1998

Membership

American Chemical Society
American Physical Society (Fellow)
American Association for the Advancement of Science (Fellow)
National Academy of Engineering

Honors and Awards

Ford Prize in High Polymer Physics administered by the Division of High Polymer Physics of the American Physical Society, 1984 (joint with F.E. Karasz)

UMass. Faculty Fellowship Award for excellence in research 1984-85

John Simon Guggenheim Memorial Foundation Fellow, 1985-86

American Chemical Society Award in Polymer Chemistry (Mobil Award), 1997

Distinguished Service Award in Advancement of Polymer Science administered by The Society of Polymer Science, Japan, 1998

Herman F. Mark Award administered by the Division of Polymer Chemistry of the American Chemical Society, 2002

Fellow, Polymer Materials Science & Engineering Division, American Chemical Society, 2004

Publications

About 340 publications and 8 patents in the field of structure-property relationships in microphase separated polymers including ionomers, polyblends and polyurethanes

Co-Author of two books:

Polymeric Sulfur and Related Polymers, 1965 (with A.V. Tobolsky)
Introduction to Polymer Viscoelasticity, 1st Edition, 1975 (J.J. Aklonis and M.C. Shen), 2nd Edition, 1983 (with J.J. Aklonis), 3rd Edition, 2005 (with M.T. Shaw)

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EXHIBITB

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Sullivan Reexamination Proceeding Control No.: 95/000,120 Filed: January 17, 2006 For: U.S. Patent No. 6,210,293)))	Examiner: Michael W. O'Neill Art Unit: 3993
In re Sullivan Reexamination Proceeding Control No.: 95/000,121 Filed: January 17, 2006 For: U.S. Patent No. 6,503,156)	Examiner: Michael W. O'Neill Art Unit: 3993
In re Sullivan Reexamination Proceeding Control No.: 95/000,122 Filed: January 17, 2006 For: U.S. Patent No. 6,506,130)	Examiner: Michael W. O'Neill Art Unit: 3993
In re Sullivan Reexamination Proceeding Control No.: 95/000,123 Filed: January 17, 2006 For: U.S. Patent No. 6,595,873)	Examiner: Michael W. O'Neill Art Unit: 3993
Central Reexamination Unit . 571-273-9900		

DECLARATION OF WILLIAM J MACKNIGHT UNDER 37 C.F.R. §1.132

I, William J. MacKnight, state as follows:

I have been asked by third party requestor Acushnet to provide a declaration in 1. connection with its Third Party Comments after Patent Owner Response to the USPTO Office actions regarding U.S. Patent Nos. 6,210,293 ("the '293 patent"), 6,503,156 ("the '156 patent"), 6,506,130 ("the '130 patent"), and 6,595,873 ("the '873 patent") (collectively the "Sullivan patents"). I have personal knowledge of the matters discussed herein, and I would testify to them under oath if called upon to do so.

- 2. I hold the position of Wilmer D. Barrett Distinguished Professor (Emeritus) in the Polymer Science and Engineering Department at the University of Massachusetts. I have been a professor at the University of Massachusetts since 1965, and was named Wilmer D. Barrett Distinguished Professor in 1998.
 - My educational background is summarized as follows:

1958: B.S. in Chemistry (with Distinction), University of Rochester

1963: M.A. in Chemistry, Princeton University

1964: Ph.D. in Physical Chemistry, Princeton University

1964: NSF Cooperative Fellow, Princeton University

- 4. I consider myself an expert in the field of polymer science, based on my years of teaching and research in that area.
- 5. I understand Acushnet has presented arguments to the USPTO regarding the patentability of the Sullivan Patents in relation to several prior art references, including U.S. Patent No. 4,431,193 to Nesbitt ("Nesbitt 193), U.S. Patent No. 5,314,187 to Proudfit ("Proudfit 187"), U.S. Patent No. 4,274,637 to Molitor ("Molitor 637"), U.S. Patent No. 5,334,673 to Wu ("Wu 673"), and U.S. Patent No. 4,674,751 to Molitor ("Molitor 751").
- 6. I was asked by Acushnet and its lawyers to direct the preparation and testing of certain golf balls that are described by the patents listed above, or combinations thereof. I have personally directed the preparation and testing of the materials and golf balls described herein.

PREPARATION OF GOLF BALLS

7. At my direction, technical personnel at Acushnet's Research and Development department created several golf balls to be tested for Shore D hardness of the outer cover layer, as measured on the surface of the ball. In particular, I directed the preparation of twelve (12) samples each of nine (9) constructions of golf balls with various combinations of core formulation and diameter, inner cover layer formulation and thickness, and outer cover layer formulation and thickness.

PREPARATION OF MATERIALS TO BE USED IN THE GOLF BALLS

8. I directed the preparation of two types of golf ball core materials. The first golf ball core material is based on the disclosure of Nesbitt 193. In particular, the core material has the following composition:

Material	Weight
Polybutadiene (BR-1220)	70.70
Polybutadiene (Taktene 220)	29.30
Zinc Diacrylate	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash	20.15
Blue Masterbatch	0.012
Luperco 231 XL	0.89

This composition is based on the core composition set forth in the Sullivan patents, for example, '293 patent, col. 16:15-30. I based this core composition on that set forth in the Sullivan patents to represent the Nesbitt 193 core for two reasons. First, Nesbitt 193 does not set forth any core composition. Second, the Sullivan patents describe balls using this core composition as "representative of the [Nesbitt] '193 patent" and as "the prior art ball of the [Nesbitt] '193 patent." See, for example, '293 patent, col. 18:33-35; col. 19:6-8. The only difference between the core composition set forth above and that set forth in the Sullivan patents as representing the Nesbitt 193 core is that the composition above does not include Papi 94, while the Sullivan patents describe using a small (0.50 by weight) amount of Papi 94 in its description of the core composition. See, for example, '293 patent, col. 16:28. I decided not to use any Papi 94 in the composition of this core because of the difficulty of obtaining the

substance and the fact that it is a dangerous substance to work with. In my opinion, based on my experience, the absence of 0.50 by weight of Papi 94 in the core composition would have negligible or no effect on any measurements of hardness of the outer cover layer of a formed ball using that core composition. I will refer to this core material herein as CORE_1.

The second golf ball core material that was prepared at my direction is based on 9. the disclosure of Proudfit 187. In particular, the core has the following composition:

Material	Weight
Polybutadiene (Taktene 220)	95.00
Vestenamer 8012	5,00
Zinc Oxide	12.20
Zinc Diacrylate	35.00
Antioxidant	0.80
Peroxide (Luperco 101 XL)	0.080
Liquid Monomer SR-351	5.00

This composition is set forth in Table 5 of Proudfit 187, col. 7: 56-68. I will refer to this core material herein as CORE_2.

- I directed the preparation of three inner cover layer materials. The first inner 10. cover layer material is based on the disclosure of Nesbitt 193. In particular, the inner cover layer material is Surlyn 8940 (formerly Surlyn 1605), which is described in Nesbitt 193, col. 3:26-30. I will refer to this inner cover layer material herein as ICL_1.
- The second type of inner cover layer material that was prepared at my direction is based on the disclosure of Molitor 637. In particular, the inner cover layer material has the following composition:

Material	Parts
Surlyn 1605 (now 8940)	88.00
Surlyn 1557 (now 9650)	17.40
TiO2 Master Batch A	35.20
Blowing Agent Master Batch B	2.32

This composition is described in Molitor 637 in Table 2, col. 14:60-65. I will refer to this inner cover layer material herein as ICL_2.

The third type of inner cover layer material that was prepared at my direction is 12. based on the disclosure of Proudfit 187. In particular, the inner cover layer material has the following composition:

Material	Blend Ratio
Surlyn 8940	75%
Surlyn 9910	25%

This composition is described in Proudfit 187 in Table 6, col. 8:25-30. I will refer to this inner cover layer material herein as ICL_3.

I directed the preparation of three outer cover layer materials. The first outer 13. cover layer material is based on the disclosure of Molitor 637. In particular, the outer cover layer material has the following composition:

Material	Parts
Estane 58133	99.7
Ficel BPA	0.3

This composition is described in Molitor 637 in Table 10, col. 18:36-41. I will refer to this outer cover layer material herein as OCL_1.

The second outer cover layer material that was prepared at my direction is based 14. on the disclosure of Wu 673. In particular, the outer cover layer material has the following composition:

Material	Grams
MDI prepolymer	100.00
Polamine 250	48.87
White dispersion	5.21

This composition is described in Wu 673 in Table I, col. 7:15-23. I will refer to this outer cover layer material herein as OCL_2.

The third outer cover layer material that was prepared at my direction is based on 15. Molitor 751. In particular, the outer cover layer material has the following composition:

Material	Parts
Texin 480 AR (now 285)	90
Surlyn 1605 (now 8940)	10
TiO2	5
Fluorescent Brightener	0.10
Antioxidant	0.17
Pigment	0.02
Release Agent	1

This composition is based on Example 4 in the Table in Molitor 751, Col. 7-8:1-24. The only difference between this cover layer composition and that disclosed as Example 4 in Molitor 751 is that Example 4 used 10 parts of Surlyn 1702 (which is now designated 9970) rather than 10 parts of Surlyn 1605 (now 8940). Surlyn 1702 (now 9970) is disclosed in Molitor 751 as

having a Shore D hardness of 62, whereas Surlyn 1605 (now 8940) is disclosed in Molitor 751 as having a Shore D hardness of 65. These Shore D hardness properties are consistent with those set forth in the Dupont data sheet for its Surlyn resins. Accordingly, in my opinion, any hardness measurements of the material disclosed in Example 4 of Molitor 751 would be even softer (i.e. lower on the Shore D scale) than such measurements of the cover layer material that was prepared at my direction. I will refer to this outer cover layer material herein as OCL_3.

PREPARATION OF GOLF BALLS

- 16. At my direction, Acushnet personnel made golf balls using the materials described above. I directed Acushnet personnel to make nine (9) constructions of golf balls, and for each type of golf ball construction, twelve (12) sample balls were made.
- 17. The first golf ball construction used the Nesbitt 193 core material (CORE_1), the Nesbitt 193 inner cover layer material (ICL_1), and the Molitor 637 outer cover layer material (OCL_1). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. This is consistent with the description in Nesbitt 193. Specifically, Nesbitt 193 describes a core and inner cover layer whose total diameter is about 1.565 inches (which is consistent with a core whose diameter is 1.495 inches and an inner cover layer whose thickness is 0.035 inches). Nesbitt 193, col. 3:26-30. Nesbitt 193 also describes an outer cover layer whose thickness is 0.0575 inches, for a total ball diameter of 1.680 inches. Nesbitt 193, col. 3:39-40. I refer to this ball construction herein as BALL_1. Twelve (12) samples of these balls were made at my direction.
- 18. The second golf ball construction used the Nesbitt 193 core material (CORE_1), the Nesbitt 193 inner cover layer material (ICL_1), and the Wu 673 outer cover layer material (OCL_2). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_2. Twelve (12) samples of these balls were made at my direction.

- 19. The third golf ball construction used the Nesbitt 193 core material (CORE_1), the Nesbitt 193 inner cover layer material (ICL_1), and the Molitor 751 outer cover layer material (OCL_3). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_3. Twelve (12) samples of these balls were made at my direction.
- 20. The fourth golf ball construction used the Nesbitt 193 core material (CORE_1), the Molitor 637 inner cover layer material (ICL_2), and the Molitor 637 outer cover layer material (OCL_1). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_4. Twelve (12) samples of these balls were made at my direction.
- 21. The fifth golf ball construction used the Nesbitt 193 core material (CORE_1), the Molitor 637 inner cover layer material (ICL_2), and the Wu 673 outer cover layer material (OCL_2). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_5. Twelve (12) samples of these balls were made at my direction.
- 22. The sixth golf ball construction used the Nesbitt 193 core material (CORE_1), the Molitor 637 inner cover layer material (ICL_2), and the Molitor 751 outer cover layer material (OCL_3). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_6. Twelve (12) samples of these balls were made at my direction.
- 23. The seventh golf ball construction used the Proudfit 187 core material (CORE_2), the Proudfit 187 inner cover layer material (ICL_3), and the Molitor 637 outer cover layer material (OCL_1). I directed Acushnet personnel to make the ball with a core

diameter of 1.5 inches, an inner cover layer thickness of 0.0375 inches, and an outer cover layer of 0.0525 inches. This is consistent with the description in Proudfit 187. Specifically, Proudfit 187 describes a core and inner cover layer whose total diameter is 1.575 inches (which is consistent with a core whose diameter is 1.5 inches and an inner cover layer whose thickness is 0.0375 inches). Proudfit 187, col. 7:43-47. Proudfit 187 also describes an outer cover layer whose thickness is 0.0525 inches, for a total ball diameter of 1.680 inches. Proudfit 187, col. 7:43-47. I refer to this ball construction herein as BALL_7. Twelve (12) samples of these balls were made at my direction.

- 24. The eighth golf ball construction used the Proudfit 187 core material (CORE_2), the Proudfit 187 inner cover layer material (ICL_3), and the Wu 673 outer cover layer material (OCL_2). I directed Acushnet personnel to make the ball with a core diameter of 1.5 inches, an inner cover layer thickness of 0.0375 inches, and an outer cover layer of 0.0525 inches. As set forth above, this is consistent with the description in Proudfit 187. I refer to this ball construction herein as BALL_8. Twelve (12) samples of these balls were made at my direction.
- 25. The ninth golf ball construction used the Proudfit 187 core material (CORE_2), the Proudfit 187 inner cover layer material (ICL_3), and the Molitor 751 outer cover layer material (OCL_3). I directed Acushnet personnel to make the ball with a core diameter of 1.5 inches, an inner cover layer thickness of 0.0375 inches, and an outer cover layer of 0.0525 inches. As set forth above, this is consistent with the description in Proudfit 187. I refer to this ball construction herein as BALL_9. Twelve (12) samples of these balls were made at my direction.
- 26. All golf balls made at my direction were made with a dimple pattern, and were painted and finished.

TESTING OF GOLF BALLS

27. I accompanied Acushnet personnel to an independent third-party plastics testing laboratory to provide the golf balls that were made at my direction for testing. The laboratory is called Plastics Technology Laboratories, Inc. (PTLI). I personally inspected the test equipment

that was to be used, and personally directed the lab technicians at PTLI as to the tests to be performed.

- 28. PTLI is accredited by the American Association for Laboratory Accreditation in the field of Mechanical Testing in accordance with the recognized International Standard ISO/IEC 17025:2005 General Requirements for the Competence of Testing and Calibration Laboratories. PTLI is specifically accredited to perform the ASTM D2240 Durometer Hardness test.
- 29. I requested that PTLI conduct Shore D hardness measurements on the surface of the formed golf balls described above. Specifically the tests to be performed would be done in accordance with ASTM D2240, with the exception that the tests would be performed on the surface of the golf balls rather than on a plaque of material as required by ASTM D2240.
- 30. Prior to conducting the Shore D measurements, PLTI technicians conditioned the balls at 40+ hours at 23 degrees (+/- 2) Celsius and 50% (+/- 5%) Relative Humidity.
- 31. PTLI conducted Shore D hardness measurements on the balls I provided to them as I requested. For each ball specimen, PTLI took five readings on the Shore D scale between the dimples of the ball. For each ball specimen, these five readings were averaged. PTLI performed this process on all twelve samples of each ball construction, and provided for each ball construction an average Shore D hardness value for all twelve samples.

RESULTS OF TESTING

- 32. Each of the twelve ball specimens that were tested for each ball construction had an average cover hardness reading of below 64 Shore D. Bach ball construction had an average cover hardness (over the twelve samples) of below 64 Shore D.
- 33. The following table sets forth the average Shore D hardness measurements (over the twelve samples) that were performed for each ball construction type:

Ball #	Core	Inner Cover Layer	Outer Cover Layer	Shore D
BALL_1	Nesbitt 193	Nesbitt 193	Molitor 637	62,0
BALL_2	Nesbitt 193	Nesbitt 193	Wu 673	56.0
BALL_3	Nosbitt 193	Nesbitt 193	Molitor 751	50.1 ¹
BALL_4	Nesbitt 193	Molitor 637	Molitor 637	61.0
BALL_5	Nesbitt 193	Molitor 637	Wu 673	55.6
BALL_6	Nesbitt 193	Molitor 637	Molitor 751	49.6
BALL_7	Proudfit 187	Proudfit 187	Molitor 637	59,4
BALL_8	Proudfit 187	Proudfit 187	Wu 673	56.8
BALL_9	Proudfit 187	Proudfit 187	Molitor 751	51.2

34. I am informed that PTLI has retained the ball samples that it tested, and they remain available for further testing if necessary. I am also informed that PTLI has retained the test results if needed.

I declare under penalty of perjury that the statements above are true and correct.

Date: May 29, 2007

William J. MacKnight

¹ As I noted above, the outer cover layer material that was tested used a slightly harder Surlyn (1605, now 8940), than the Surlyn described in Example 4 of Molitor 751, so the hardness measurements using the outer cover layer material of Example 4 would be even softer than those set forth for Molitor 751 in this table.

IN THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF DELAWARE

CERTIFICATE OF SERVICE

I, David E. Moore, hereby certify that on June 1, 2007, a true and correct copy of the within document was caused to be served on the attorney of record at the following addresses as indicated:

VIA HAND DELIVERY

Thomas L. Halkowski Fish & Richardson P.C. 919 N. Market Street, Suite 1100 P. O. Box 1114 Wilmington, DE 19899-1114

VIA ELECTRONIC MAIL

Frank E. Scherkenbach Fish & Richardson P.C. 225 Franklin Street Boston, MA 02110-2804 scherkenbach@fr.com

Robert A. Denning David S. Shuman Fish & Richardson P.C. 12290 El Camino Real San Diego, CA 92130 denning@fr.com shuman@fr.com

/s/ David E. Moore

Richard L. Horwitz David E. Moore Potter Anderson & Corroon LLP Hercules Plaza - Sixth Floor 1313 North Market Street Wilmington, DE 19899-0951 (302) 984-6000 rhorwitz@potteranderson.com dmoore@potteranderson.com

721875 / 30030

Exhibit B To Dalton Declaration



Flexural Report Page 1 of 4

Testing : Flexural Properties Of Plastics ASTM D790-03 Procedure A Test Method

P20071713 Project Number

Acushnet Company Customer

: Troy Lester Attention Attachments: 1 Page Of Photos Analyst : L. Howland : May 22, 2007

: Tested as received Sample Preparation

: 0.497" x 0.128" x 6.00" (Average) Sample Dimensions

: ASTM Flex Bar Sample Type

Span Length (in) : 2.080 Cross-Head Speed (in/min) : 0.055 Span-To- Depth Ratio : 16±1:1 Radius Of Supports (in) : 0.197 Radius Of Loading Nose (in) : 0.197

Date

Conditioning 40+ hours at 23°C ± 2°C / 50% ± 5% RH

23°C ± 2°C / 50% ± 5% RH **Test Conditions**

: ASTM D 790 specifies modulus and strength be reported to 3 significant figures Significance

		Flexural Stress At 5% Strain	Flexural Modulus (tangent*) (PSI)
Sample Name	Test Number	(PSI)	(F3I)
MDI Prepolymer	1	596	13600
• • • • • • • • • • • • • • • • • • • •	2	473	11200
	3	573	13100
	. 4	523	12100
	5	, 536	12300
	Ayerage	540	12500
	Std. Dev.	47	929
Estonia Blend	1	729	16900
	2	711	16100
	3	726	16600
	4	763	17600
	5	704	16100
	Average	727	16700
	Std. Dev.	23	627

^{* =} computer generated curve fit

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Flexural Report Page 2 of 4

Testing : Flexural Properties Of Plastics
Test Method : ASTM D790-03 Procedure A

Project Number : P20071713
Customer : Acushnet Company
Attention : Troy Lester
Analyst : L. Howland
Date : May 22, 2007

ACCREDITED Cort. No. 0518.01

Sample Preparation : Tested as received

Sample Dimensions : 0.498" x 0.131" x 6.00" (Average)

Sample Type : ASTM Flex Bar

Span Length (in) : 2.080
Cross-Head Speed (in/min) : 0.055
Span-To- Depth Ratio : 16±1:1
Radius Of Supports (in) : 0.197
Radius Of Loading Nose (in) : 0.197

Conditioning : 40+ hours at 23°C ± 2°C / 50% ± 5% RH

Test Conditions : 23°C ± 2°C / 50% ± 5% RH

Significance : ASTM D 790 specifies modulus and strength be reported to 3 significant figures

		Flexural Stress At 5% Strain	Flexural Modulus (tangent*)
Sample Name	Test Number	(PSI)	(PSI)
8940	1	2180	50800
	2	2160	51200
	3	2160	50300
	4	2140	48100
	5	2170	50000
	Average	2160	50100
	Std. Dev.	15	1200
Texin Blend	1	267	5120
I WALLE DELIVERING	2	268	5150
	3	264	5120
	4	247	4750
	5	282	5370
	Average	266	5100
	Std. Dev.	13	223

^{* =} computer generated curve fit

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Flexural Report Page 3 of 4

Testing : Flexural Properties Of Plastics Test Method ASTM D790-03 Procedure A

Project Number : P20071713 Customer **Acushnet Company** Attention Troy Lester Analyst L. Howland

Date : May 22, 2007

Sample Preparation : Tested as received

Sample Dimensions : 0.499" x 0.130" x 6.00" (Average)

Sample Type : ASTM Flex Bar

Span Length (in) : 2,080 Cross-Head Speed (in/min) : 0.055 Span-To- Depth Ratio : 16±1:1 Radius Of Supports (in) 0.197 Radius Of Loading Nose (in) : 0.197

Conditioning : 40+ hours at 23°C ± 2°C / 50% ± 5% RH

Test Conditions : 23°C ± 2°C / 50% ± 5% RH

Significance : ASTM D 790 specifies modulus and strength be reported to 3 significant figures

	·	Flexural Stress At 5% Strain	Flexural Modulus (tangent*)
Sample Name	Test Number	(PSI)	(PSI)
Blend 2	1	2380	56800
	2	2360	54700
	3	2340	54800
	4	2400	55900
	5	2430	57700
	Average	2380	56000
	Std. Dev.	35	1290
Blend 3	1	2330	54500
	2	2320	53B0D
	3	2280	52300
	4	2250	51200
	5	2300	52800
	Average	2300	52900
	Std. Dev.	32	1290

^{* =} computer generated curve fit

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Flexural Report Page 4 of 4

Testing : Flexural Properties Of Plastics
Test Method : ASTM D790-03 Procedure A

Project Number : P20071713
Customer : Acushnef Company
Attention : Troy Lester

Analyst : L. Howland
Date : May 22, 2007

Sample Preparation : Tested as received

Sample Dimensions : 0.499" x 0.131" x 6.00" (Average)

Sample Type : ASTM Flex Bar

 Span Length (in)
 : 2,080

 Cross-Head Speed (in/min)
 : 0.055

 Span-To- Depth Ratio
 : 16±1:1

 Radius Of Supports (in)
 : 0.197

 Radius Of Loading Nose (in)
 : 0.197

Conditioning : 40+ hours at 23°C ± 2°C / 50% ± 5% RH

Test Conditions : 23°C ± 2°C / 50% ± 5% RH

Significance : ASTM D 790 specifies modulus and strength be reported to 3 significant figures

Sample Name	Test Number	Flexural Stress At 5% Strain (PSI)	Flexural Modulus (tangent *) (PSI)
Blend 4	1	2180	50300
	2	2210	50900
	3	2110	48700
	4	2170	49200
	5	2190	50000
	Average	2170	49800
	Std. Dev.	38	876

* = computer generated curve fit

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Photos Report Page 1 of 1

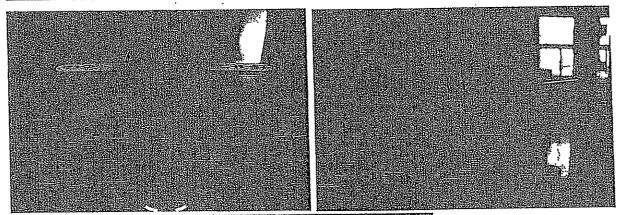
Testing : Flexural Properties Of Plastics
Test Method : ASTM D790-03 Procedure A

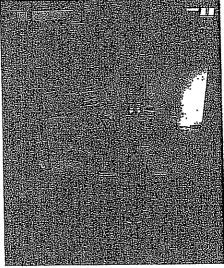
Project Number : P20071713

Customer : Acushnet Company

Attention : Troy Lester
Analyst : L. Howland
Date : May 22, 2007







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AC0131406

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Durometer Hardness Report Page 1 of 7

Rubber Property - Durometer Hardness Testing

ASTM D2240-05 - Modified test specimen - golf ball Test Method

P20071713 Project Number **Acushnet Company** Customer

Troy Lester Attention J. McCartny Analyst

May 22, 2007 Date

Attachments: 1 Page Of Photos

Specimen Preparation Test Location

Tested Thickness

Durometer Type Indention Time Interval

Indenter Used

Conditioning

Test Conditions Significance

Tested as received Tested between dimples N/A

Zwick Digital 7206.07 (Shore D S/N 110129) 1.0 Second

40+ hours at 23°C ± 2°C / 50% ± 5% RH 23°C ± 2°C / 50% ± 5% RH

Per ASTM D2240, readings below 20 or above 90 are not considered reliable.

Set 1	1	2	Reading 3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID							4.4	er-a
1	60.5	62.5	59.9	58.7	59.7	60,3	1.4	2.3
Ż.	59.9	61.5	61.1	62.1	59.9	60.9	10	1.6
2 3	62.3	61.9	62.7	61.3	62.5	62.1	0.6	0.9
4	64.5	64.3	63.5	61.7	63,3	63.5	1_1	1.7
ś	64.1	63.1	62.5	63.7	62.5	63.2	0.7	1.1
5 6 7 8	62.5	64.1	62.5	59.9	60,9	62.0	1.6	2.6
7	64.1	62.7	63.1	63.3	63.9	63.4	0.6	0:9-
Ŕ	61.7	62.3	61.9	€2.9	625	62.3	0:5	-0.8
9	61.9	62,1	59.9	62,1	59.9	61.2	1.2	1.9
10	61.9	62.1	61.5	61.3	61.3	61.6	0.4	0.6
11	60.9	62.1	61.7	63.5	60.9	61.8	1.1	1.7
12	60.5	62.3	61.9	61.9	60.5	61.4	0,9	1.4
12	03.0							
					Overall Totals	62.6	1.3	2.1
•			· · · · · · · · · · · · · · · · · · ·					
. Set 2		_	Reading	4	5	Average	Std. Dev.	C.O.V. (%)
	1	2	3	4	v	Vicialic	O(0, D0).	0,011, (10,
Golf Ball ID					en e	57.6	0.6	1.0
1	56.9	57.5	57.5	57.7	58.5	56.7	0.4	. 0.7
2 3	56.7	56.1	57.1	56.9	56.9		0.6	1.0
3	56.5	57.3	56.1	56.5	57.5	56.8	0.5	1.0
4	57.7	57.5	57.1	56.3	56.9	57.1		0.8
4 5 6 .	57.3	56.3	56.9	57.5	56.9	57.0	0.5	
6 .	55.1	55.7	55.9	56.5	55.7	55.8	0,5	0.9
7	49.9	50.5	50.7	50.3	51.1	50.5	0.4	0.9
8	54.5	55.1	55.9	54.9	55.1	55,1	0.5	0,9
9	54.7	53.5	53.9	54.3	54.1	54.1	0.4	0.8
10	56.3	57.7	58.3	57.5	56.9	57,3	0.8	1.3
11	56.1	56,9	57.1	56.3	56.1	56.5	0.5	0.8
12	57.3	56.3	56.7	57.1	56.9	56.9	0.4	0.7
					Overall Totals	56.0	2.0	3.5

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AC0131407

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Durometer Hardness Report Page 2 of 7

Rubber Property - Durometer Hardness

Testing Test Method ASTM D2240-05 - Modified test specimen - golf ball

Project Number P20071713 **Acushnet Company** Customer Troy Lester J. McCarthy Attention Analyst May 22, 2007 Date

ACCREDITED

Specimen Preparation

Test Location N/A

Tested Thickness Durometer Type

Indention Time Interval Indenter Used

Conditioning

Test Conditions Significance

Tested as received Tested between dimples

Zwick Digital 7206.07 (Shore D S/N 110129)

1.0 Second

40+ hours at 23°C ± 2°C / 50% ± 5% RH

23°C ± 2°C / 50% ± 5% RH

Per ASTM D2240, readings below 20 or above 90 are not considered reliable.

Set 3	1	2	Reading 3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID								4.5
1	53.5	51.7	51.7	52,1	52.7	52:3	0.8	1.5
2	50.5	51.1	51.3	50.3	50.1	50.7	0.5	1.0
2 3	49.1	49.7	49.5	49.3	49.6	49,4	0.2	0.5
4	53.1	51.3	50.9	51.9	53.9	52.2	1.3	2.4
5	50.1	49.8	49.7	49.1	48.9	49,5	0:5	1.0
4 5 6 7 8 9	48.5	49.3	48,7	50.1	49.3	49.2	0,6	1.3
7	49.1	49.5	49,7	49.7	48.9	49.4	0.4	0.7
8	49.7	50.1	49,3	49.5	50.1	49.7	0.4	0.7
9	49.1	49.7	50.1	48.9	50.1	49.6	0.6	1.1
10	50.5	50.3	49.7	49.7	50.5	50.1	0.4	0.8
11	48.7	49.1	48.9	50.7	50,5	49.6	0.9	1.9
12	49.5	49.7	48.9	50.2	49.1	49.5	0.5	1.0
					Overall Totals	50.1	1.2	2.4
Set 4			Reading					
5 51 7	1	2	3	4	5	Average	Sid. Dev.	C.O.V. (%)
Golf Ball ID	•							
	5B.9	59.7	59,5	61.5	62.1	60.3	1.4	2.3
ົ່ງ	59.7	59.9	59.7	58.9	59.3	59.5	0.4 ·	0.7
1 2 3 4	61.3	59.7	59.1	61.3	61.7	60.6	1.1	1.9
ă	60.1	61.3	59.7	60.9	59.9	60.4	0,7	1.1
5	61.1	63.3	61.3	61.5	61.9	61.8	. 0.9	1.4
5 6 7	61.3	62.3	60.3	61.3	64.1	61.9	1.4	2.3
ž	59.9	62.5	61.9	63.1	63.7	62,2	1.5	2.3
Ř	61.1	59,3	61.5	60.9	61.5	60.9	0.9	1.5
B 9	61.7	60.1	61.7	62.7	61.5	61.5	9.0	1.5
10	61.1	59.7	61.1	60.1	6D.1	60.4	0,6	1.1
11	60.7	60.1	63,3	59.3	59.7	60.6	1.6	2.6
12	63.3	61.7	60.9	61.3	61.7	61.8	0.9	1.5
					Overall Totals	61.0	1.3	2.1

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Durometer Hardness Report Page 3 of 7

Rubber Property - Durometer Hardness Testing

ASTM D2240-05 - Modified test specimen - golf ball Test Method

P20071713 Project Number **Acushnel Company** Customer Troy Lester Attention J. McCarthy Analyst Date May 22, 2007

Tested as received Tested between dimples

Test Location N/A **Tested Thickness**

Specimen Preparation

Zwick Digital 7206.07 (Shore D S/N 110129) **Durometer Type**

1.0 Second Indention Time Interval "D"

Indenter Used 40+ hours at 23°C ± 2°C / 50% ± 5% RH 23°C ± 2°C / 50% ± 5% RH Conditioning

Test Conditions

Per ASTM D2240, readings below 20 or above 90 are not considered reliable. Significance

Set 5			Reading	4	5	Average	Std. Dev.	C.O.V. (%)
	1	2	3	4	J	Atomyo	0.4. 2011	
Golf Ball ID		50 F	FO 0	52.5	53,1	52.7	0.3	0.6
1	52.3	52.5	52.9	57.1	57.3	57.3	0:4	0.6
2	56.9	57.7	57.7		57.3 52.7	54.3	1.9	3,5
3	53.3	53.7	57.5	54.3		55.4	0.9	1.6
4	54.5	55.1	54.9	56.7	55.9	56.3	1.1	1.9
2 3 4 5 6 7 8 9	54.7	56.3	56.1	57.7	56.5		0.4	-0.6-
6	56.7	56.1	56.3	56.9	56.9	56.6		-2.1
7	54.9	52.7	52.9	54.7	52.7	53.6	1.1	1:8
8	57.1	56.9	56.9	54.7	55.9	56.3	1:0	
9	55.5	55.3	56.7	54.9	55.7	55.6	0.7	1.2
10	55.9	56.1	57.3	55.7	57.3	56,5	8.0	1.4
11	55.9	56.3	56.1	56.1	56.9	56.3	0.4	0.7
12	56.1	56.7	56.5	56.1	55. 9	56.3	0.3	0.6
					Overail Totals	55.6	1.6	2.8
			Techion					
Set 6	1	2	Reading 3	· 4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID	•	_	-	-		-		
	50.3	49.3	50.1	51.3	51.5	50.5	0,9	1.8
1	51.0	51.5	50.7	48.7	49.1	50.2	1.2	2.4
2	49.7	51.1	49.5	49.1	50.3	49.9	0.8	1.6
3	51.3	49.9	49.7	5D.1	50.7	50.3	0.7	1.3
4		49.9	49.9	4B.1	50.7	49.3	1.2	2.4
2 3 4 5 6 7 8	48.1	48.7	49.1	50.5	48.9	49.1	0.8	1.7
5	48.3		49.5	50.1	49.9	49.6	0.4	0.8
7	49.1	49.5			49.3	49.7	0.5	1.1
8	50.5	50.1	49.3	49.5 50.3	49.9	49.6	0.5	1.1
9	49.5	48.9	49.5		49.5 46.5	47.7	1.1	2.3
10	48.5	48.5	48.5	46.5		49,9	0.8	1.5
11	49.5	49.5	51,3	49.7	49.7		1.3	2.7
12	51.1	50.9	48.1	48.7	49.3	49.6	1.5	£1
					Overall Totals	49.6	1.1	2.2

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Durometer Hardness Report Page 4 of 7

Rubber Property - Durometer Hardness ASTM D2240-05 - Modified test specimen - golf ball Testing Test Method

Project Number P20071713 Customer **Acushnet Company** Troy Lester Attention

Analyst J. McCarthy May 22, 2007 Date

Tested as received Specimen Preparation Tested between dimples **Test Location**

N/A Tested Thickness Zwick Digital 7206.07 (Shore D S/N 110129) Durometer Type

Indention Time Interval 1.0 Second

Indenter Used "D"

40+ hours at 23°C ± 2°C / 50% ± 5% RH Conditioning

Test Conditions

23°C ± 2°C / 50% ± 5% RH
Per ASTM D2240, readings below 20 or above 90 are not considered reliable. Significance

Set 7			Reading					
	1	2	3	4	5	Average	Sid. Dev.	C.O.V. (%)
Golf Ball ID								
1	59.3	59.3	62.3	62.1	63.1	61.2	1.8	2.9
	60.3	6D.3	59.5	61.1	58. 9	60.0	8.0	1.4
3	56.1	57.1	56.9	58.9.	57.5	57:3	1.0	1.8
4	61.5	60.9	62.3	60.3	60.5	61.1	0.8	1.3
5	56.7	55.5	55.5	-55:9.	57.9	56.3	1:D	1:8
2 3 4 5 6 7 8 9	60.7	60.7	60.9	59:5	59.1	60.2_	8.0	1.4
7	59.5	60.3	59.9	60.7	-59.7	60.0	0:5	70.8
8	60.3	60.5	60.1	60.7	59.5	60,2	0.5	0:8
9	58.3	57.9	58.5	5B.5	<i>57.</i> 9	58.2	0.3	0.5
10	58.9	61.3	62.5	61.5	60.5	60.9	1,3	2.2
iĩ	60.3	59.3	57.7	58.5	58.7	58,9	1.0	1.6
12	59.3	60.5	60.1	58.3	58. 9	59.4	0.9	1.5
					Overall Totals	59.5	1.7	2.9
Set 8			Reading					
	1	2	3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID	•							
1	58.1	56.7	55.5	55.9	56.1	55.5	1.0	1.8
ż	55.7	58.3	56.9	57.3	. 55.3	56.7	1.2	21
2 3	57.1	53.9	58.7	54.7	58.1	56,5	2.1	3,7
4.	56.9	57.3	58.1	58.3	58.9	57.9	0.8	1.4
Ś	54.9	55.3	55.5	58.3	5 5.9	56.2	1.4	2.5
6	56,3	54.3	53.9	53.9	54.9	54.7	1.0	1.B
7	58.1	56.7	56.9	55.1	58.5	57.1	1.3	2.3
R	58.3	56.1	57.1	55.9	55.3	56,5	1.2	2.1
4 5 6 7 8 9	58.1	57.3	57.5	59.1	57.5	57.9	0.7	1.3
10	56.5	57.3	59.5	56.5	56.7	57.3	1.3	2.2
	00,0				55.3	54,5	0.6	1.1
3.1	53.9	54.3	54.9	54.3	20,0	U-4,-U	U.U	
11 12	53,9 55,2	54.3 56.1	54.9 55.3	54.1 54.5		55.3	0.6	1.0
12	53,9 55,2	54.3 56.1	54.9 55.3	54.1	55.5			

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Durometer Hardness Report Page 5 of 7

Rubber Property - Durometer Hardness Testing

ASTM D2240-05 - Modified test specimen - golf ball Test Method

Project Number P20071713 **Acushnet Company** Customer **Troy Lester** Attention J. McCarthy Analyst May 22, 2007 Date

Tested as received Specimen Preparation Tested between dimples Test Location

Significance

N/A **Tested Thickness** Zwick Digital 7206.07 (Shore D S/N 110129) Durometer Type Indention Time Interval 1.0 Second

"D" Indenter Used

40+ hours at 23°C ± 2°C / 50% ± 5% RH 23°C ± 2°C / 50% ± 5% RH Conditioning **Test Conditions** Per ASTM D2240, readings below 20 or above 90 are not considered reliable.

Set 9	4		Reading . 3	4	5	Average	Std. Dev.	C.O.V. (%)
	1	2	3	4	3	Menage	Old. Doi:	
Golf Ball ID	45.7	40.0	End	49.5	48.7	49.2	0.6	1.3
1 2 3 4 5 6 7	48.5	49,3	50:1		46.1°	47.2	0.7	1.5
2	47.5	46.9	47.7	47:9		47.4	1.1	2.3
3	46.5	46.9	49.1	46,7	47.9	48.4	1.3	2.8
4	47.7	47.5	47.1	50.1	49.5		0.9	1.8
5	47.9	50.3	48.5	48.7	-48.7·	48.8	0.4	0.9
6	49.3	49.3	49.9	49.5	50.3	49.7		1.2
7	48.9	49.3	49.1	49.3	47.9	48:9	0,6	
В	49,1	48.9	47.9	50.1	47:9	48.8	0,9	1.9
8 9	47.1	44.7	44.5	44.7	45.7	45.3	1.1	2.4
10	48.1	47.1	46.1	48.5	46.7	47.3	1.0	2.1
11	47.1	47.3	4B.5	47.9	47.7	47.7	0.5	1.1
12	45.9	46.3	46.5	45.3	47.3	46.3	0.7	1.6
					Overall Totals	47.9	1.5	3.1
Set 10			Reading					
Get 10	1	2	3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID	•	•						. m
1	58.1	58.5	59.5	60.7	59.5	59.3	1.0	1.7
	61.5	62.3	60.9	61.9	61.3	61.6	0.5	0.9
2 3 4 5 6	59.1	58.5	60.7	58,3	58.7	59.1	1.0	1.6
Ā	57.3	59.5	56.7	57.7	57.5	57 <i>.</i> 7	1.1	1.8
, E	58.1	63.1	57.7	59.7	58.3	59.4	2.2	3.7
ě	56.7	56,9	57.3	57.9	56.9	57,1	0.5	8.0
7	58,9	59.3	60.3	58.9	60.5	59,6	8.0	1.3
8	57.3	59.9	56.7	59,3	62.1	59.1	2.2	3.7
9	59.5	57.9	58.1	61.7	57.3	58,9	1.8	3.0
	60.9	61.1	59.9	61.3	59.7	60.6	0,7	1.2
10	61.1	60.7	61.3	60.3	60.3	60.7	0.5	8.0
11 12	60.5	58.5	60.3	61.1	60.1	69.1	1.0	1.6
₹ €aa		-	-		Overall Totals	59.4	1.6	2,8

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Durometer Hardness Report Page 6 of 7

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Rubber Property - Durometer Hardness ASTM D2240-05 - Modified test specimen - golf ball Testing Test Method

P20071713 Project Number **Acushnet Company** Customer Troy Lester Attention J. McCarthy Analyst Date May 22, 2007

Specimen Preparation Tested as received Test Location Tesled between dimples NA

Tested Thickness Durometer Type Zwick Digital 7206.07 (Shore D S/N 110129)

1.0 Second Indention Time Interval Indenter Used

Conditioning

Test Conditions

40+ hours at 23°C \pm 2°C / 50% \pm 5% RH 23°C \pm 2°C / 50% \pm 5% RH Per ASTM D2240, readings below 20 or above 90 are not considered reliable. Significance

Set 11	1	2	Reading 3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID	•	2,	w		~			
Guii baii iu	55 ₅ 5.	-54.3	58.5	56.5	55.5-	56.1	1:6	2.8
,	55,3	54.9	55:5=	54.3	55.1	55.0	0.5	8.0
2	56.9	5B.1	56.9	57.1	56.5	57.1	7076	1.1
ž	56.5	56.7	55.9	56,3	55.7	56.2	0.4	0.7
F.	55,9	56.4	55:9-	56.3	56.1	56.1	0.2	0.3
2 3 4 5 6 7 8	58.5	57.7	57.1	56.3	58.1	57.5	0:8,	1.5
7	59,3	60.7	59.1	-58:5	58.5	59.2	0,9	1.5
Ŕ	57.5	56.5	56.1	58:5	.58.1	57.3	1.0	1.8
9	56.9	56.1	57.1	56.5	55.5	56.4	0,6	1.1
10	56.5	55.7	56.5	57,5	58.3	56.9	- 1.0	1.8
11	57.3	58.1	58.5	56.9	56.7	57.5	8.0	1.3
12	55.9	56.1	56.7	56.5	55,5	56.1	0.5	0.9
124	00.0	02						
					Overali Totals	56.8	1.3	2.2
Set 12			Reading		_		out new	0.037.00
	1	2	3	4	5	Average	Stu. Dev.	C.O.V. (%)
Golf Ball ID						70.0	4.4	20
1	48. 9	49.3	49.5	52.3	51.1	50.2	1.4	2.9 1.7
2	49.9	51.5	51.3	51.1	52.3	51.2	0.9	
3	49.3	53.3	52.1	50.1	49.5	50.9	1.8	3,5
4	48.7	47.9	50.3	51.5	52,7	50.2	2.0	3.9
2 3 4 5 6 7	49.9	51.9	52.9	52.3	50.3	51,5	1,3	2.5
6	4B.9	51.0	49.3	51.5	51.3	50.4	1.2	2.4
7	52.1	50.1	49.5	51.9	50.5	50.8	1.1	2.2
8	53.5	52.9	52.1	52.5	52,5	52.7	0,5	1.0
9	51.9	53.5	51.9	51.1	52.7	52.2	0,9	1.7
10	51.3	52.9	52.5	51.3	52.3	52.1	0.7	1.4
11	51.9	51.1	49.1	50.3	53.5	51,2	1.7	3.2
12	51.1	50.9	51.1	50,1	50.3	50.7	0.5	0.9
					Overall Totals	51.2	1.4	. 27

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Durometer Hardness Report Page 7 of 7

Rubber Property - Durometer Hardness

Testing Test Method ASTM D2240-05 - Modified test specimen - golf ball P20071713 Project Number. Acushnet Company Customer Troy Lester Attention

J. McCarthy Analyst May 22, 2007 Date

Specimen Preparation Tested as received Tested between dimples Test Location

NA **Tested Thickness** Zwick Digital 7206.07 (Shore D S/N 110129) Durometer Type

1.0 Second Indention Time Interval Indenter Used

40+ hours at 23°C ± 2°C / 50% ± 5% RH Conditioning

23°C ± 2°C / 50% ± 5% RH
Per ASTM D2240, readings below 20 or above 90 are not considered reliable. **Test Conditions** Significance

Wilson Ultra Tour Balata 90 Bo	x 93007 1	2	Reading 3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID Sample #1 Sample #2: 1 3-1 3-2 3-3	61.9 56.3 55.1 62.1 64.7 60.7	62.3 54.9 56.1 62.1 61.7 62.3	62.1 55.1 56.9 60.1 62.7 63.3	-63:1 56:1 57:3 60:7 61:7 60:7	61.9 56.3 55.5 61.7 62.1 62.5	62.3 55.7 56.2 61.3 62.0 61.9	0.5 0.7 0.9 0.9 0.4 1.2	0.8 1.2 1.6 1.5 0.7 1.9
					Overall Totals	59.9	2.9	4.9

Wilson Ultra Tour Balata 90 -	New Box 1	2	Reading 3	4	5	Average	Std. Dev.	C.O.V. (%)
Golf Ball ID 2-1 2-2 2-3 3-1 3-2 3-3 4-1 4-2 4-3	63.3 59.7 59.3 61.5 62.1 60.5 60.1 59.5 61.1	61.7 60.3 59.1 61.3 60.3 61.1 60.5 60.1	60.7 60.1 58.7 61.9 63.1 62.1 61.1 59.9 60.9	60.7 60.1 59.9 62.1 63.3 60.5 60.9 61.3	61.5 59.7 60.1 60.5 62.9 61.3 60.1 59.9 61.1	61.6 69.0 59.4 61.5 62.3 61.1 60.5 60.1 60.9	1.1 0.3 0.6 0.6 1.2 0.7 0.5 0.7	1.7 0.4 1.0 1.0 2.0 1.1 0.8 1.1
					Overall Totals	60.8	1.1	1.8

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Durometer Hardness Report Page 1 of 1

Rubber Property - Durometer Hardness ASTM D2240-05 Testing

Test Method Project Number P20071713 Customer **Acushnet Company** Attention Troy Lester-J. McCarthy Analyst May 22, 2007 Date



Tested as received - One reading per disk, five disks per sample Specimen Preparation

No Sample Piled See Below **Tested Thickness** Disk

Sample Type Zwick Digital 7205.07 (Shore D S/N 110129) **Durometer Type**

1.0 Second Indention Time Interval Indenter Used "D"

40+ hours at 23°C \pm 2°C / 50% \pm 5% RH 23°C \pm 2°C / 50% \pm 5% RH Conditioning

Test Conditions

Per ASTM D2240, readings below 20 or above 90 are not considered reliable. Significance

			Reading					
Sample ID	1	2	3	4	5	Average	Std. Dev.	C.O.V. (%)
MDI Prepolymer	51.9	52.1	52.1	54.9	50.1	51.6	0.9	1.7
Estonia Blend	57.3	56.3	55.3	56.7	56.1	56.5	0.5	8.0
894D	63:1	63.5	.64.5	63.1	65.1	63.9	0.9	1.4
Texin Blend	39.9	40.7	38.9	38,5	39,7	39.5	0.9	2.2
Blend 2	63.5	64.1	64.9	65,9	65.3	64.7	1.0	1.5
Blend 3	64:5	64.5	64.5	64.1	64.1	64.3	0.2	0.3
Blend 4	64.1	63.3	65.5	64.1	64.9	64.4	8.0	1.3
					Overall Totals	57.9	9.0	15.5

Thickness (in)

MDI Prepolymer	0,349
Estonia Blend	0.259
8940	0,259
Texin Blend .	0.259
Blend 2	0.260
Blend 3	0.261
Blend 4	0.249

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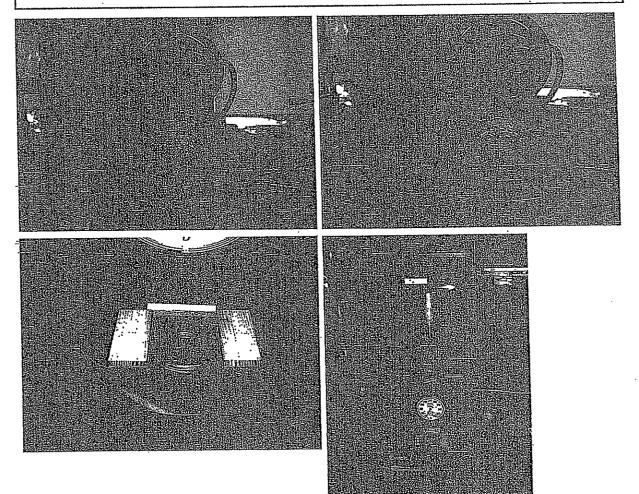


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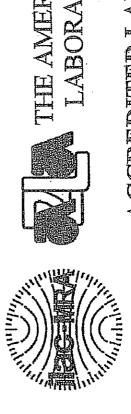
Testing : Rubber Property - Durometer Hardness
Test Method : ASTM D2240-05

Test Method : ASTM D2240-05
Project Number : P20071713
Customer : Acushnet Company
Attention : Troy Lester
Analyst : J. McCarthy
Date : May 22, 2007





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for technical competence in the field of

Mechanical Testing

competence for a defined scope and the operation of a laboratory quality management system (refer to joint ISO-ILAC-IAF. This laboratory is Accredited in accordance with the recognized International Standard ISO/IEC 17025;2005 General Requirements for the Competence of Testing and Calibration Laboratories. This Acoroditation demonstrates technical Presented this 22nd day of February 2007. Communiqué datéd 18 June 2005).

CORPORAS ES LA SERIE LA SERIE

President
For the Accreditation Council
Certificate Number 619.01
Valid to February 28, 2009

For the tests or types of tests to which this Accreditation applies, please refer to the laboratory's Mechanical Scope of Accreditation.

HIGHLY CONFIDENTIAL SUBJECT TO PROTECTIVE ORDER

SCOPE OF ACCREDITATION TO ISO/IEC 17025:2005

PLASTICS TECHNOLOGY LABORATORIES, INC. 50 Pearl Street Pittsfield, MA 01201 James Koehler Phone: 413 499 0983 Web address: www.ptli.com

MECHANICAL

Valid To: February 28, 2009

Certificate Number: 0619-01

In recognition of the successful completion of the A2LA evaluation process, accreditation is granted to this laboratory to perform the following tests on plastics and polymers, rubber and rubber products, composites, films, packaging.

Test Standard	Test Description
ASTM D149	Dielectric Strength, Dielectric Breakdown: Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies
ASTM D150	Dielectric Constant, Dissipation Factor, Loss Factor, Dc/Df: Standard Test Methods for AC Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulation
ASTM D256	Notched Izod Impact: Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics
ASTM D257	Volume / Surface Resistivity: Standard Test Methods for DC Resistance or Conductance of Insulating Materials
ASTM D395	Compression Set: Standard Test Methods for Rubber Property—Compression Set Method B
ASTM D412	Tensile Strength Of Rubber, Elastomer Tensile: Standard Test Methods for Vulcanized Rubber and Thermoplastic Blastomers—Tension
ASTM D471	Volume Change, Fluid Resistance, Swell: Standard Test Method for Rubber Property-Effect of Liquids
ASTM D523	60° Gloss, 60 Degree Gloss, Sheen: Standard Test Method for Specular Gloss
ASTM D542	$\it Refractive\ Index$. Standard Test Method for Index of Refraction of Transparent Organic Plastics
ASTM D543	Chemical Computibility: Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents
ASTM D570	Water Absorption, 24 Hour H_2O Absorption: Standard Test Method for Water Absorption of Plastics
ASTM D573	Oven Aging: Standard Test Method for Rubber-Deterioration in an Air Oven
ASTM D618	Conditioning of Plastics: Standard Practice for Conditioning Plastics for Testing

Test Standard	Test Description
ASTM D624	Tear Strength, Die C Tear: Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers
ASTM D635	Flammability, Horizontal Burn: Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position
ASTM D638	Tensile Test of Plastics, ASTM Tensile Properties, Tensile Modulus, Elongation, Tensile Strength: Standard Test Method for Tensile Properties of Plastics
ASTM D648	Heat Deflection Temperature, HDT, DTUL, Deflection Temperature Under Load: Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position
ASTM D695	Compression Test, Compressive Properties, Compression Strength, Compression Modulus: Standard Test Method for Compressive Properties of Rigid Plastics
ASTM D696	Coefficient Of Linear Thermal Expansion -30°C To +30°C, CTE, Dilatometer. Standard Test Method for Coefficient of Linear Thermal Expansion of Plastics Between -30°C and 30°C With a Vitreous Silica Dilatometer
ASTM D732	Shear Strength, Shear Strength By Puncture: Standard Test Method for Shear Strength of Plastics by Punch Tool
ASTM D785	Rockwell Hardness (M, R, E Scales): Standard Test Method for Rockwell Hardness of Plastics and Electrical Insulating Materials
ASTM-D789	Relative Viscosity, Nylon: Standard Test Methods for Determination of Relative Viscosity of Polyamide (PA)
ASTM-D790	Flexural Test, Three Point Bending, Four Point Bending: Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials
ASTM D792	Specific Gravity, Relative Density, Density, Apparent Density: Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement
ASTM D882	Tensile Test - Thin Sheeting, Film Tensile, Film Modulus: Standard Test Method for Tensile Properties of Thin Plastic Sheeting
ASTM D903	Peel Strength, 180 Degree Peel: Standard Test Method for Peel or Stripping Strength of Adhesive Bonds
ASTM D955	Mold Shrinkage: Standard Test Method of Measuring Shrinkage from Mold Dimensions of Thermoplastics, (Type A & B)
ASTM D1002	Lap Shear, Bond Strength: Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)
ASTM D1003	Haze and Luminous Transmittance, Diffuse Transmittance: Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics
ASTM D1004	Tear Resistance, Film Tear: Standard Test Method for Initial Tear Resistance of Plastic Film and Sheeting

Test Standard	Test Description
ASTM D1204	Dimensional Stability, Linear Dimensional Stability: Standard Test Method for Linear Dimensional Changes of Nonrigid Thermoplastic Sheeting or Film at Elevated Temperature
ASTM D1238	Melt Flow Rate, MFR, Melt Index, MI: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer
ASTM D1243	Dilute Solution Viscosity: Standard Test Method for Dilute Solution Viscosity of Vinyl Chloride Polymers
ASTM D1525	Vicat Softening Temperature, VST: Standard Test Method for Vicat Softening Temperature of Plastics
ASTM D1603	Carbon Black Content: Standard Test Method for Carbon Black In Olefin Plastics
ASTM D1622	Apparent Density: Standard Test Method for Apparent Density of Rigid Cellular Plastics
ASTM D1693	Stress-Cracking, ESCR Of Polyethylene: Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics
ASTM D1708	Tensile Test, Micro Tensile: Standard Test Method for Tensile Properties of Plastics By Use of Microtensile Specimens
ASTM D1709	Drop-Dart Test, Film Impact, Film Dart Drop: Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method
ASTM D1822	Tensile Impact: Standard Test Method for Tensile-Impact Energy to Break Plastics and Electrical Insulating Materials
ASTM D1894	Coefficient of Friction, COF, Static COF, Kinetic COF: Standard Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting
ASTM D1922	Tear Resistance, Elmendorf Tear: Standard Test Method for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method
ASTM D1938	Trouser Tear: Standard Test Method for Tear-Propagation Resistance (Trouser Tear) of Plastic Film and Thin Sheeting by a Single-Tear Method
ASTM D2240	Durometer Hardness (A & D), Shore Hardness, Shore Durometer: Standard Test Method for Rubber Property—Durometer Hardness.
ASTM D2244	Color, CIE Hunter: Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates
ASTM D2344	Short Beam Shear, Interlaminar Shear: Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates
ASTM D2565	Xenon Arc Accelerated Weathering, Artificial Weathering: Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications
ASTM D2583	Barcol Hardness, Indenter Hardness: Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor
ASTM D2584	Ignition Loss, Glass Content, Fiber Content, Ash Content, Resin Content: Standard Test Method for Ignition Loss of Cured Reinforced Resins
ASTM D2734	Void Content, Method A: Standard Test Methods for Void Content of Reinforced Plastics

Test Standard	Test Description
ASTM D2857	Viscosity, Dilute Solution Viscosity, Intrinsic Viscosity, Inherent Viscosity: Standard Practice for Dilute Solution Viscosity of Polymers
ASTM D2863	Oxygen Index, OI, Limiting Oxygen Index, LOI: Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)
ASTM D3163	Lap-Shear, Bond Strength: Standard Test Method for Determining Strength of Adhesively Bonded Rigid Plastic Lap-Shear Joints in Shear by Tension Loading
ASTM D3167	Peel Test, Floating Roller Peel: Standard Test Method for Floating Roller Peel Resistance of Adhesives
ASTM D3170	Chip Resistance, Gravelometer: Standard Test Method for Chipping Resistance of Coatings
ASTM D3171	Acid Digestion, Void Content By Acid Digestion: Standard Test Methods for Constituent Content of Composite Materials, Procedures A, B, C, D, E, G
ASTM D3359	Cross Hatch Adhesion: Standard Test Methods for Measuring Adhesion by Tape Test
ASTM D3418	Tg, Glass Transition Temperature by DSC: Standard Test Method for Transition Temperatures of Polymers By Differential Scanning Calorimetry
ASTM D3574-A	Density: Standard Test Methods for Flexible Cellular Materials—Slab, Bonded, and Molded Urethane Foams
ASTM D3574-E	Tensile Properties: Standard Test Methods for Flexible Cellular Materials—Slab, Bonded, and Molded Urethane Foams
ASTM D3574-F	Tear Resistance: Standard Test Methods for Flexible Cellular Materials—Slab, Bonded, and Molded Urethane Foams
ASTM D3763	Dynatup, Instrumented Impact: Standard Test Method for High Speed Puncture Properties of Plastics Using Load and Displacement Sensors
ASTM D3801	Flammability, Vertical Burn: Standard Test Method for Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position
ASTM D3835	Capillary Rheometry, Melt Viscosity, Thermal Stability, Apparent Viscosity: Standard Test Method for Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer
ASTM D4060	Taber Abrasion: Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser
ASTM D4226	Impact Resistance, Gardner Impact, Drop Dart Impact: Standard Test Methods for Impact Resistance of Rigid Poly(Vinyl Chloride) (PVC) Building Products
ASTM D4329	UV Exposure, QUV Exposure: Standard Practice for Fluorescent UV Exposure of Plastics
ASTM D4440	Dynamic Mechanical Analysis, DMA, Parallel Plate Rheology, Steady State Shear: Standard Test Method for Plastics: Dynamic Mechanical Properties: Melt Rheology
ASTM D4459	Xenon-Arc: Indoor Accelerated Sunlight Exposure: Standard Practice for Xenon-Arc Exposure of Plastics Intended for Indoor Applications

Test Standard

Test Description

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ASTM D4587	UV Exposure, QUV: Standard Practice for Fluorescent UV-Condensation Exposures of Paint and Related Coatings
ASTM D4812	Unnotched Impact, Unnotched Izod: Standard Test Method for Unnotched Cantilever Beam Impact Strength of Plastics
ASTM D5048-B	Burning Characteristics and Resistance to Burn Through of Solid Plastics: Standard Test Method for Measuring the Comparative Burning Characteristics and Resistance to Burn-Through of Solid Plastics Using 125-mm Flame
ASTM D5132	Horizontal Burn Rate: Standard Test Method for Horizontal Burning Rate of Polymeric Materials Used in Occupant Compartments of Motor Vehicles
ASTM D5279	DMA in Torsion, Shear Modulus, Storage Modulus, Tan Delta, Tg: Standard Test Method for Plastics: Dynamic Mechanical Properties: In Torsion
ASTM D5379	Shear of Composite, V-Notch Shear, Iosipescu Shear: Standard Test Method for Shear Properties of Composite Materials by the V-Notched Beam Method
ASTM D5420	Impact Resistance, Gardner Impact, Drop Dart Impact: Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact)
ASTM D5628	Impact Resistance, Gardner Impact, Drop Dart Impact: Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimens by Means of a Falling Dart (Tup or Falling Mass)
ASTM D5630	Ash Content: Standard Test Method for Ash Content in Thermoplastics
ASTM D6110	Charpy Impact of Notched Samples: Standard Test Method for Determining the Charpy Impact Resistance of Notched Specimens of Plastics
ASTM D6272	Flexural Property, Four Point Flex, Four Point Bending: Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials by Four-Point Bending
ASTM D6290	Color Analysis: Standard Test Method for Color Determination of Plastic Pellets
ASTM D6869	Karl Fischer, Water Content, Moisture Content By Karl Fischer Titration: Standard Test Method for Coulometric and Volumetric Determination of Moisture in Plastics Using the Karl Fischer Reaction (the Reaction of Iodine with Water)
ASTM E96	Water Vapor Transmission, WVTR: Standard Test Methods for Water Vapor Transmission of Materials
ASTM E313	Yellowness Index: Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates
ASTM E793	DSC, Delta H, Heat of Fusion, Crystallinity: Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry
ASTM E831	TMA, CTE, Coefficient Of Thermal Expansion, Tg By TMA: Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis
ASTM E1131	TGA, Carbon Black Content By TGA, Ash Content: Standard Test Method for Compositional Analysis by Thermogravimetry

Test Standard	Test Description
ASTM E1252	FTIR, Material ID, Basic Material Identification: Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis
ASTM E1269	DSC, Specific Heat: Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry
ASTM E1347	Color Analysis, Tristimulus Color: Standard Test Method for Color and Color- Difference Measurement by Tristimulus (Filter) Colorimetry
ASTM E1356	DSC, Tg, Glass Transition Temperature By DSC: Standard Test Method for Assignment of the Glass Transition Temperatures by Differential Scanning Calorimetry
ASTM E1545	TMA, Tg By TMA, Glass Transition Temperature By TMA: Standard Test Method for Assignment of the Glass Transition Temperature by Thermomechanical Analysis
ASTM E1868	LOD By TGA, Weight Loss: Standard Test Method for Loss-On-Drying by Thermogravimetry
ASTM F1306	Slow Rate Penetration: Standard Test Method for Slow Rate Penetration Resistance of Flexible Barrier Films and Laminates
ASTM G151	QUV UV Exposure: Standard Practice for Exposing Nonmetallic Materials in Accelerated Test Devices that Use Laboratory Light Sources
ASTM G154	QUV: UV Exposure: Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials
ASTM G155	Xenon Arc, Accelerated Weathering: Standard Practice for Operating Xenon. Arc Light Apparatus for Exposure of Non-Metallic Materials
ISO 34-1	Tear Strength: Rubber, Vulcanized or Thermoplastic — Determination of Tear Strength — Part 1: Method B Using an Angle Test Piece With or Without a Nick of Specified Depth
ISO 37	Tensile Strength: Rubber, Vulcanized or Thermoplastic — Determination of Tensile Stress-Strain Properties
ISO 62	Water Absorption, H_2O Absorption; Plastics — Determination of Water Absorption
ISO 75	Heat Deflection Temperature, HDT: Plastics — Determination of Temperature of Deflection Under
ISO 178	Flexural Properties, Flexural Stress, Flexural Modulus: Determination of Flexural Properties
ISO 179-1	Charpy Impact Strength: Plastics — Determination of Charpy Impact Properties — Part 1: Non-Instrumented Impact Test
ISO 180	Izod Impact: Plastics Determination of Izod Impact Strength
ISO 188	Accelerated Aging in an Oven: Rubber, vulcanized or thermoplastic
ISO 291	Conditioning of Plastics: Plastics - Standard Atmospheres for Conditioning and Testing
ISO 306	Vicat Softening Temperature, VST: Plastics — Thermoplastic Materials — Determination of Vicat Softening Temperature (VST)

Test Standard	Test Description
ISO 489	Refractive Index, RI, Index of Refraction: Plastics - Determination of Refractive Index
ISO 527	Tensile Properties, Tensile Modulus, Tensile Strength: Plastics — Determination of Tensile
ISO 604	Compression Properties, Compressive Strength, Compressive Modulus: Plastics — Determination of Compressive Properties
ISO 815	Compression Set: Rubber, Vulcanized or Thermoplastic — Determination of Compression Set At Ambient, Elevated or Low Temperatures
ISO 868	Hardness, Shore A & D: Plastics and Ebonite — Determination of Indentation Hardness by Means of A Durometer (Shore Hardness)
ISO 1133	Melt Flow Rate, Melt Volume Rate: Plastics — Determination of The Melt Mass-Flow Rate (MFR) and The Melt Volume-Flow Rate (MVR) of Thermoplastics
ISO 1183-1	Density, Specific Gravity: Plastics - Methods for Determining The Density of Non-Cellular Plastics - Part 1: Method A Immersion Method
ISO 1817	Volume Swell: Rubber, Vulcanized - Determination of The Effect of Liquids
ISO 2039-2	Hardness, Rockwell: Plastics — Determination of Hardness — Part 2: Rockwell Hardness (M, R, E Scales)
ISO 3451	Ash Content, Percent Ash: Plastics - Determination of Ash
ISO 3795	Flammability: Road Vehicles, and Tractors and Machinery for Agriculture and Forestry – Determination of Burning Behaviour of Interior Materials
ISO 4589-2	Oxygen Index: Plastics — Determination of Burning Behaviour by Oxygen Index Part 2: Ambieut-Temperature Test
ISO 4892-3	QUV, UV Exposure: Plastics — Methods of Exposure To Laboratory Light Sources — Part 3: Fluorescent UV Lamps
ISO 6383-2	Tear Resistance of Film: Determination of tear resistance — Part 2: Elmendorf method
ISO 6452	Fogging: Rubber or Plastics Coated Fabrics — Determination of Fogging Characteristics of Trim Materials In The Interior Of Automobiles
ISO 6603-2	Dynatup, Multiaxial Impact: Plastics — Determination of Puncture Impact Behaviour of Rigid Plastics — Part 2: Instrumented Impact Testing
ISO 7765	Drop Dart, Dynatup: Plastics Film and Sheeting — Determination of Impact Resistance by The Free-Falling Dart Method — Part 1: Staircase Methods; Part 2: Instrumented Puncture Test
ISO 8009-9	Tensile Properties of Contraceptives: Mechanical contraceptives - Reusable natural and silicone rubber confraceptive diaphragms - Section 9 of requirements and tests
ISO 11357	DSC, Glass Transition Temperature, Tg, Crystallinity, Delta H, Heat of Fusion: Plastics — Differential Scanning Calorimetry (DSC)
ISO 11358	TGA, Change In Mass, Thermal Residue: Plastics — Thermogravimetry (TG) of Polymers — General Principles

Test Standard	Test Description
ISG 11359	TMA, CTE, Coefficient of Thermal Expansion, Glass Transition Temperature by TMA, Tg by TMA, Penetration Temperature by TMA: Plastics—Thermomechanical Analysis (TMA)
ISO 11443	Shear Viscosity: Plastics — Determination of The Fluidity of Plastics Using Capillary and Slit-Die Rheometers
ISO 15512	Karl Fischer, Water Content, Moisture Content By Karl Fischer Titration: Plastics — Determination of Water Content Method B Water Vaporization
	Test Standards Other Than ASTM And ISO Methods
49 CFR 571.302	Flammability: Code of Federal Regulations Title 49: Transportation CFR Part 571 Federal Motor Vehicle Standards Section 302 Flammability of Interior Materials Also Identified As FMVSS 302
DIN 75 201	Fogging: Determination of the Windscreen Fogging Characteristics of Trim Materials in Motor Vehicles
EIA 564	Polycarbonate Chemical Compatibility
GM9059P	Thermal Oxidative Stability: Test for Thermal-Oxidative Stability Characteristics of Plastics
GM9305P	Fogging: Criteria for Determining Acceptable/Nonacceptable Materials
GM9900P	Solvent Resistance, Chemical Compatibility: Cleaning/Solvent Resistance of Automotive Components During Normal Customer Use
IEC 60093	Volume and Surface Resistivity: Methods of Test for Volume Resistivity and Surface Resistivity of Solid Electrical Insulating Materials
IEC 60243	Dielectric Strength: Electrical Strength of Insulating Materials — Test Methods — Part 1: Tests at Power Frequencies
IEC 60250	Dielectric Constant, Dissipation Factor, Loss Factor: Recommended Methods for The Determination of The Permittivity and Dielectric Dissipation Factor of Electrical Insulating Materials At Power, Audio and Radio Frequencies Including Metre Wavelengths
MIL-STD -3010A	Test Method 2065 Puncture Resistance: Supercedes Canceled Document - FTMS 101C-2065.1 Puncture Resistance and Elongation Test (1/8 Inch Radius Probe Method)
SAE J369	Horizontal Flame Test: Flammability of Polymeric Interior Materials—Horizontal Test Method
SAE J400	Chip Resistance, Gravelometer: Test for Chip Resistance of Surface Coatings
SAE J1756	Fogging: Test Procedure To Determine The Fogging Characteristics of Interior Automotive Materials
SAE J1885	Xenon Arc Accelerated Weathering, Artificial Weathering: Accelerated Exposure of Automotive Interior Trim Components Using A Controlled Irradiance Water Cooled Xenon-Arc Apparatus

Test Standard	Test Description
SAE J1960	Xenon Arc Accelerated Weathering, Artificial Weathering: Accelerated Exposure of Automotive Exterior Materials Using a Controlled Irradiance Water-Cooled Xenon-Arc Apparatus
SAE J2020	QUV: Accelerated Exposure of Automotive Exterior Materials Using a Fluorescent UV and Condensation Apparatus
SAE J2236	Temperature Resistance: Standard Method for Determining Continuous Upper Temperature Resistance of Elastomers
UL-94	Flammability: Tests For Flammability of Plastic Materials for Parts in Devices and Appliances

EXHIBIT 7

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Sullivan Reexamination Proceeding Control No.: 95/000,120 Filed: January 17, 2006 For: U.S. Patent No. 6,210,293)))) .	Examiner: Michael W. O'Neill Art Unit: 3993
In re Sullivan Reexamination Proceeding Control No.: 95/000,121 Filed: January 17, 2006 For: U.S. Patent No. 6,503,156)	Examiner: Michael W. O'Neill Art Unit: 3993
In re Sullivan Reexamination Proceeding Control No.: 95/000,122 Filed: January 17, 2006 For: U.S. Patent No. 6,506,130)	Examiner: Michael W. O'Neill Art Unit: 3993
In re Sullivan Reexamination Proceeding Control No.: 95/000,123 Filed: January 17, 2006 For: U.S. Patent No. 6,595,873)	Examiner: Michael W. O'Neill Art Unit: 3993
Central Reexamination Unit . 571-273-9900		

DECLARATION OF WILLIAM J MACKNIGHT UNDER 37 C.F.R. §1.132

I, William J. MacKnight, state as follows:

1. I have been asked by third party requestor Acushnet to provide a declaration in connection with its Third Party Comments after Patent Owner Response to the USPTO Office actions regarding U.S. Patent Nos. 6,210,293 ("the '293 patent"), 6,503,156 ("the '156 patent"), 6,506,130 ("the '130 patent"), and 6,595,873 ("the '873 patent") (collectively the "Sullivan patents"). I have personal knowledge of the matters discussed herein, and I would testify to them under oath if called upon to do so.

- I hold the position of Wilmer D. Barrett Distinguished Professor (Emeritus) in the 2. Polymer Science and Engineering Department at the University of Massachusetts. I have been a professor at the University of Massachusetts since 1965, and was named Wilmer D. Barrett Distinguished Professor in 1998.
 - My educational background is summarized as follows: 3.

1958: B.S. in Chemistry (with Distinction), University of Rochester

1963: M.A. in Chemistry, Princeton University

1964: Ph.D. in Physical Chemistry, Princeton University

1964: NSF Cooperative Fellow, Princeton University

- I consider myself an expert in the field of polymer science, based on my years of 4. teaching and research in that area.
- I understand Acushnet has presented arguments to the USPTO regarding the 5. patentability of the Sullivan Patents in relation to several prior art references, including U.S. Patent No. 4,431,193 to Nesbitt ("Nesbitt 193), U.S. Patent No. 5,314,187 to Proudfit ("Proudfit 187"), U.S. Patent No. 4,274,637 to Molitor ("Molitor 637"), U.S. Patent No. 5,334,673 to Wu ("Wu 673"), and U.S. Patent No. 4,674,751 to Molitor ("Molitor 751").
- I was asked by Acushnet and its lawyers to direct the preparation and testing of certain golf balls that are described by the patents listed above, or combinations thereof. I have personally directed the preparation and testing of the materials and golf balls described herein.

PREPARATION OF GOLF BALLS

At my direction, technical personnel at Acushnet's Research and Development department created several golf balls to be tested for Shore D hardness of the outer cover layer, as measured on the surface of the ball. In particular, I directed the preparation of twelve (12) samples each of nine (9) constructions of golf balls with various combinations of core formulation and diameter, inner cover layer formulation and thickness, and outer cover layer formulation and thickness.

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PREPARATION OF MATERIALS TO BE USED IN THE GOLF BALLS

I directed the preparation of two types of golf ball core materials. The first golf 8. ball core material is based on the disclosure of Nesbitt 193. In particular, the core material has the following composition:

Material	Weight
Polybutadiene (BR-1220)	70.70
Polybutadiene (Taktene 220)	29.30
Zinc Diacrylate	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash	20.15
Blue Masterbatch	0.012
Luperco 231 XL	0.89

This composition is based on the core composition set forth in the Sullivan patents, for example, '293 patent, col. 16:15-30. I based this core composition on that set forth in the Sullivan patents to represent the Nesbitt 193 core for two reasons. First, Nesbitt 193 does not set forth any core composition. Second, the Sullivan patents describe balls using this core composition as "representative of the [Nesbitt] '193 patent" and as "the prior art ball of the [Nesbitt] '193 patent." See, for example, '293 patent, col. 18:33-35; col. 19:6-8. The only difference between the core composition set forth above and that set forth in the Sullivan patents as representing the Nesbitt 193 core is that the composition above does not include Papi 94, while the Sullivan patents describe using a small (0.50 by weight) amount of Papi 94 in its description of the core composition. See, for example, '293 patent, col. 16:28. I decided not to use any Papi 94 in the composition of this core because of the difficulty of obtaining the

substance and the fact that it is a dangerous substance to work with. In my opinion, based on my experience, the absence of 0.50 by weight of Papi 94 in the core composition would have negligible or no effect on any measurements of hardness of the outer cover layer of a formed ball using that core composition. I will refer to this core material herein as CORE_1.

The second golf ball core material that was prepared at my direction is based on the disclosure of Proudfit 187. In particular, the core has the following composition:

Material	Weight
Polybutadiene (Taktene 220)	95.00
Vestenamer 8012	5.00
Zinc Oxide	12.20
Zinc Diacrylate	35.00
Antioxidant	0.80
Peroxide (Luperco 101 XL)	0.080
Liquid Monomer SR-351	5.00

This composition is set forth in Table 5 of Proudfit 187, col. 7: 56-68. I will refer to this core material herein as CORE_2.

- I directed the preparation of three inner cover layer materials. The first inner 10. cover layer material is based on the disclosure of Nesbitt 193. In particular, the inner cover layer material is Surlyn 8940 (formerly Surlyn 1605), which is described in Nesbitt 193, col. 3:26-30. I will refer to this inner cover layer material herein as ICL_1.
- The second type of inner cover layer material that was prepared at my direction is based on the disclosure of Molitor 637. In particular, the inner cover layer material has the following composition:

Material	Parts
Surlyn 1605 (now 8940)	88.00
Surlyn 1557 (now 9650)	17.40
TiO2 Master Batch A	35.20
Blowing Agent Master Batch B	2.32

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This composition is described in Molitor 637 in Table 2, col. 14:60-65. I will refer to this inner cover layer material herein as ICL_2.

The third type of inner cover layer material that was prepared at my direction is 12. based on the disclosure of Proudfit 187. In particular, the inner cover layer material has the following composition:

Material	Blend Ratio
Surlyn 8940	75%
Surlyn 9910	25%

This composition is described in Proudfit 187 in Table 6, col. 8:25-30. I will refer to this inner cover layer material herein as ICL_3.

I directed the preparation of three outer cover layer materials. The first outer 13. cover layer material is based on the disclosure of Molitor 637. In particular, the outer cover layer material has the following composition:

Material	Parts
Estane 58133	99.7
Ficel EPA	0.3

This composition is described in Molitor 637 in Table 10, col. 18:36-41. I will refer to this outer cover layer material herein as OCL_1.

14. The second outer cover layer material that was prepared at my direction is based on the disclosure of Wu 673. In particular, the outer cover layer material has the following composition:

Material	Grams
MDI prepolymer	100.00
Polamine 250	48.87
White dispersion	5.21

This composition is described in Wu 673 in Table I, col. 7:15-23. I will refer to this outer cover layer material herein as OCL_2.

15. The third outer cover layer material that was prepared at my direction is based on Molitor 751. In particular, the outer cover layer material has the following composition:

Material	Parts
Texin 480 AR (now 285)	90
Surlyn 1605 (now 8940)	10
TiO2	5
Fluorescent Brightener	0.10
Antioxidant	0.17
Pigment	0.02
Release Agent	1

This composition is based on Example 4 in the Table in Molitor 751, Col. 7-8:1-24. The only difference between this cover layer composition and that disclosed as Example 4 in Molitor 751 is that Example 4 used 10 parts of Surlyn 1702 (which is now designated 9970) rather than 10 parts of Surlyn 1605 (now 8940). Surlyn 1702 (now 9970) is disclosed in Molitor 751 as

having a Shore D hardness of 62, whereas Surlyn 1605 (now 8940) is disclosed in Molitor 751 as having a Shore D hardness of 65. These Shore D hardness properties are consistent with those set forth in the Dupont data sheet for its Surlyn resins. Accordingly, in my opinion, any hardness measurements of the material disclosed in Example 4 of Molitor 751 would be even softer (i.e. lower on the Shore D scale) than such measurements of the cover layer material that was prepared at my direction. I will refer to this outer cover layer material herein as OCL_3.

PREPARATION OF GOLF BALLS

- At my direction. Acushnet personnel made golf balls using the materials 16. described above. I directed Acushnet personnel to make nine (9) constructions of golf balls, and for each type of golf ball construction, twelve (12) sample balls were made.
- The first golf ball construction used the Nesbitt 193 core material (CORE_1), the 17. Nesbitt 193 inner cover layer material (ICL_1), and the Molitor 637 outer cover layer material (OCL 1). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. This is consistent with the description in Nesbitt 193. Specifically, Nesbitt 193 describes a core and inner cover layer whose total diameter is about 1.565 inches (which is consistent with a core whose diameter is 1.495 inches and an inner cover layer whose thickness is 0.035 inches). Nesbitt 193, col. 3:26-30. Nesbitt 193 also describes an outer cover layer whose thickness is 0.0575 inches, for a total ball diameter of 1.680 inches. Nesbitt 193, col. 3:39-40. I refer to this ball construction herein as BALL_1. Twelve (12) samples of these balls were made at my direction.
- The second golf ball construction used the Nesbitt 193 core material (CORE 1), 18. the Nesbitt 193 inner cover layer material (ICL_1), and the Wu 673 outer cover layer material (OCL 2). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_2. Twelve (12) samples of these balls were made at my direction.

- The third golf ball construction used the Nesbitt 193 core material (CORE_1), the 19. Nesbitt 193 inner cover layer material (ICL_1), and the Molitor 751 outer cover layer material (OCL_3). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_3. Twelve (12) samples of these balls were made at my direction.
- The fourth golf ball construction used the Nesbitt 193 core material (CORE_1), 20. the Molitor 637 inner cover layer material (ICL_2), and the Molitor 637 outer cover layer material (OCL 1). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_4. Twelve (12) samples of these balls were made at my direction.
- The fifth golf ball construction used the Nesbitt 193 core material (CORE_1), the Molitor 637 inner cover layer material (ICL_2), and the Wu 673 outer cover layer material (OCL 2). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL 5. Twelve (12) samples of these balls were made at my direction.
- The sixth golf ball construction used the Nesbitt 193 core material (CORE_1), 22. the Molitor 637 inner cover layer material (ICL_2), and the Molitor 751 outer cover layer material (OCL_3). I directed Acushnet personnel to make the ball with a core diameter of 1.495 inches, an inner cover layer thickness of 0.035 inches, and an outer cover layer of 0.0575 inches. As set forth above, this is consistent with the description in Nesbitt 193. I refer to this ball construction herein as BALL_6. Twelve (12) samples of these balls were made at my direction.
- The seventh golf ball construction used the Proudfit 187 core material 23. (CORE 2), the Proudfit 187 inner cover layer material (ICL_3), and the Molitor 637 outer cover layer material (OCL_1). I directed Acushnet personnel to make the ball with a core

diameter of 1.5 inches, an inner cover layer thickness of 0.0375 inches, and an outer cover layer of 0.0525 inches. This is consistent with the description in Proudfit 187. Specifically, Proudfit 187 describes a core and inner cover layer whose total diameter is 1.575 inches (which is consistent with a core whose diameter is 1.5 inches and an inner cover layer whose thickness is 0.0375 inches). Proudfit 187, col. 7:43-47. Proudfit 187 also describes an outer cover layer whose thickness is 0.0525 inches, for a total ball diameter of 1.680 inches. Proudfit 187, col. 7:43-47. I refer to this ball construction herein as BALL_7. Twelve (12) samples of these balls were made at my direction.

- 24. The eighth golf ball construction used the Proudfit 187 core material (CORE_2), the Proudfit 187 inner cover layer material (ICL_3), and the Wu 673 outer cover layer material (OCL_2). I directed Acushnet personnel to make the ball with a core diameter of 1.5 inches, an inner cover layer thickness of 0.0375 inches, and an outer cover layer of 0.0525 inches. As set forth above, this is consistent with the description in Proudfit 187. I refer to this ball construction herein as BALL_8. Twelve (12) samples of these balls were made at my direction.
- 25. The ninth golf ball construction used the Proudfit 187 core material (CORE_2), the Proudfit 187 inner cover layer material (ICL_3), and the Molitor 751 outer cover layer material (OCL_3). I directed Acushnet personnel to make the ball with a core diameter of 1.5 inches, an inner cover layer thickness of 0.0375 inches, and an outer cover layer of 0.0525 inches. As set forth above, this is consistent with the description in Proudfit 187. I refer to this ball construction herein as BALL_9. Twelve (12) samples of these balls were made at my direction.
- 26. All golf balls made at my direction were made with a dimple pattern, and were painted and finished.

TESTING OF GOLF BALLS

27. I accompanied Acushnet personnel to an independent third-party plastics testing laboratory to provide the golf balls that were made at my direction for testing. The laboratory is called Plastics Technology Laboratories, Inc. (PTLI). I personally inspected the test equipment

that was to be used, and personally directed the lab technicians at PTLI as to the tests to be performed.

- 28. PTLI is accredited by the American Association for Laboratory Accreditation in the field of Mechanical Testing in accordance with the recognized International Standard ISO/IEC 17025:2005 General Requirements for the Competence of Testing and Calibration Laboratories. PTLI is specifically accredited to perform the ASTM D2240 Durometer Hardness test.
- 29. I requested that PTLI conduct Shore D hardness measurements on the surface of the formed golf balls described above. Specifically the tests to be performed would be done in accordance with ASTM D2240, with the exception that the tests would be performed on the surface of the golf balls rather than on a plaque of material as required by ASTM D2240.
- 30. Prior to conducting the Shore D measurements, PLTI technicians conditioned the balls at 40+ hours at 23 degrees (+/- 2) Celsius and 50% (+/- 5%) Relative Humidity.
- 31. PTLI conducted Shore D hardness measurements on the balls I provided to them as I requested. For each ball specimen, PTLI took five readings on the Shore D scale between the dimples of the ball. For each ball specimen, these five readings were averaged. PTLI performed this process on all twelve samples of each ball construction, and provided for each ball construction an average Shore D hardness value for all twelve samples.

RESULTS OF TESTING

- 32. Each of the twelve ball specimens that were tested for each ball construction had an average cover hardness reading of below 64 Shore D. Each ball construction had an average cover hardness (over the twelve samples) of below 64 Shore D.
- 33. The following table sets forth the average Shore D hardness measurements (over the twelve samples) that were performed for each ball construction type:

Ball#	Core	Inner Cover Layer	Outer Cover Layer	Shore D
BALL_1	Nesbitt 193	Nesbitt 193	Molitor 637	62,0
BALL_2	Nesbitt 193	Nesbitt 193	Wu 673	56.0
BALL_3	Nesbitt 193	Nesbitt 193	Molitor 751	50.1
BALL_4	Nesbitt 193	Molitor 637	Molitor 637	61.0
BALL_5	Nesbitt 193	Molitor 637	Wu 673	55,6
BALL_6	Nesbitt 193	Molitor 637	Molitor 751	49.6
BALL_7	Proudfit 187	Proudfit 187	Molitor 637	59,4
BALL_8	Proudfit 187	Proudfit 187	Wu 673	56.8
BALL_9	Proudfit 187	Proudfit 187	Molitor 751	51.2

I am informed that PTLI has retained the ball samples that it tested, and they 34. remain available for further testing if necessary. I am also informed that PTLI has retained the test results if needed.

I declare under penalty of perjury that the statements above are true and correct.

Date: May 29, 2007

Teellean Free They William J. MacKnight

¹ As I noted above, the outer cover layer material that was tested used a slightly harder Surlyn (1605, now 8940), than the Surlyn described in Example 4 of Molitor 751, so the hardness measurements using the outer cover layer material of Example 4 would be even softer than those set forth for Molitor 751 in this table.

EXHIBIT 8

US005542677A

United States Patent [19]

Sullivan et al.

Patent Number: [11]

5,542,677

Date of Patent: [45]

Aug. 6, 1996

[54] (GOLF	BALL	COVER	COMPOSITIONS
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[75] Inventors: Michael J. Sullivan, Chicopee, Mass.; Robert A. Weiss, Storrs, Conn.

[73] Assignee: Lisco, Inc., Tampa, Fla.

[21] Appl. No.: 359,620

Dec. 20, 1994

[22] Filed:

273/DIG. 4; 525/201; 525/221

...... 526/318.45; 273/235 R, Field of Search 273/DIG. 22, DIG. 4; 525/201, 221

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Primary Examiner-Joseph L. Schofer Assistant Examiner-N. Sarofim

[57] ABSTRACT

The present invention is directed to golf ball cover compositions containing blends of high or low carboxylic acid based copolymers and ethylene copolymers such as ethylene alkyl acrylates. The carboxylic acid groups of the blends are neutralized with metal cations. Golf balls produced with the cover molded thereon exhibit desired properties of distance and high coefficient of restitution without substantially sacrificing and/or improving characteristics like playability and durability when compared to existing covers comprising ionomeric resin blends.

2 Claims, No Drawings

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GOLF BALL COVER COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to metal cation neutralized blends of acid copolymers with non-acid functional polymers such as ethylene acrylates, and to improved golf ball covers made from these blends. The improved golf ball covers are useful for producing golf balls, particularly multi-piece balls, exhibiting essentially the desired travel distance while maintaining or improving the playability and/or durability characteristics necessary for repetitive play.

BACKGROUND OF THE INVENTION

Ionomeric resins are polymers containing interchain ionic bonding. As a result of their toughness, durability, and flight characteristics, various ionomeric resins sold by E.I. DuPont de Nemours & Company under the trademark "Surlyn®" and more recently, by the Exxon Corporation (see U.S. Pat. No. 4,911,451) under the trademarks "Escor®", and the tradename "Iotek", have become the materials of choice for the construction of golf ball covers over the traditional "balata" (trans polyisoprene, natural or synthetic) rubbers. The softer balata covers, although exhibiting enhanced playability properties, lack the durability properties required for repetitive play.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid or maleic acid. In some instances, an additional softening comonomer can also be included to form a terpolymer. The pendent ionic groups in the ionomeric resins interact to form ion-rich aggregates contained in a non-polar polymer matrix. The metal ions, such as sodium, zinc, magnesium, lithium, potassium, calcium, etc. are used to neutralize some portion of the acid groups in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e. improved durability, etc. for golf ball construction over balata

Broadly, the ionic copolymers comprise one or more alpha-olefins and from about 9 to about 30 weight percent of alpha, beta-ethylenically unsaturated mono- or dicarboxylic acid, the basic copolymer neutralized with metal ions to the extent desired. Usually, at least 20% of the carboxylic acid groups of the copolymer are neutralized by the metal ions (such as sodium, potassium, manganese, zinc, lithium, calcium, nickel, magnesium, and the like) and exist in the ionic state. In general, ionic copolymers including up to 16% acid are considered "low acid" ionomers, while those including greater than 16% acid are considered "high acid" ionomers by the present inventors.

Suitable olefins for use in preparing the ionomeric resins include ethylene, propylene, butene-1, hexene-1, and the 55 like. Unsaturated carboxylic acids include acrylic, methacrylic, ethacrylic, α -chloroacrylic, crotonic, maleic, furnaric, iraconic acids, and the like. The ionomeric resins utilized in the golf ball industry are generally copolymers of ethylene with acrylic (i.e. Escor®) and/or methacrylic (i.e. Surlyn®) acid. In addition, two or more types of ionomeric resins may be blended into the cover compositions in order to produce the desired properties of the resulting golf balls.

Along this line, the properties of the cover compositions and/or the ionomeric resins utilized in the golf ball industry 65 vary according to the type and amount of the metal cation, the molecular weight, the composition of the base resin (i.e.

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the nature and the relative content of the olefin, the unsaturated carboxylic acid groups, etc.), the amount of acid, the degree of neutralization and whether additional ingredients such as reinforcement agents or additives are utilized. Consequently, the properties of the ionomer resins can be controlled and varied in order to produce golf balls having different playing characteristics, such as differences in hardness, playability (i.e. spin, feel, click, etc.), durability (i.e. impact and/or cut resistance), and resilience (i.e. coefficient of restitution).

However, while there are currently more than fifty commercial grades of ionomers available from DuPont and Exxon with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e. relative content of ethylene and methacrylic and/or acrylic acid groups), the degree of neutralization and additive ingredients such as reinforcement agents, etc., a great deal of research continues in order to develop golf ball cover compositions exhibiting not only the playability characteristics previously associated with the balata cover, but also the improved impact resistance and carrying distance properties produced by the ionomeric resins. Thus, an object of the present invention is to provide golf ball cover compositions which, when utilized in golf ball construction, produce balls exhibiting improved travel distance while maintaining satisfactory playability and durability properties such as coefficient of restitution (C.O.R.).

A golf ball's coefficient of restitution (C.O.R.) is the ratio of the relative velocity of the ball after direct impact to that before impact. One way to measure the coefficient of restitution is to propel a ball at a given speed against a hard massive surface, and measure its incoming velocity and outgoing velocity. The coefficient of restitution is defined as the ratio of the outgoing velocity to incoming velocity of a rebounding ball and is expressed as a decimal. As a result, the coefficient of restitution can vary from zero to one, with one being equivalent to an elastic collision and zero being equivalent to an inelastic collision.

The coefficient of restitution of a one-piece golf ball is a function of the ball's composition. In a two-piece or a multi-layered golf ball, the coefficient of restitution is a function of the core, the cover and any additional layer. While there are no United States Golf Association (U.S.G.A.) limitations on the coefficient of restitution values of a golf ball, the U.S.G.A. requires that the golf ball cannot exceed an initial velocity of 255 feet/second. As a result, golf ball manufacturers generally seek to maximize the coefficient of restitution of a ball without violating the velocity limitation.

In various attempts to produce a high coefficient of restitution golf ball exhibiting the enhanced travel distance desired, the golfing industry has blended various ionomeric resins. However, many of these blends do not exhibit the durability and playability characteristics necessary for repetitive play and/or the enhanced travel distance desired.

It is, therefore, desirable to develop golf ball cover compositions which produce golf balls exhibiting properties of desired carrying distance (i.e., possess desirable coefficient of restitution values) over known ionomeric cover blends such as those set forth in U.S. Pat. Nos. 4,884,814 and 4,911,451, without sacrificing or improving playability and/or durability characteristics.

Furthermore, while as stated above, Surlyn® and Escor® (i.e. "Totek") are materials of choice for golf ball cover construction when balata is not used, these materials are relatively costly. It has, therefore, become desirable to

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develop a low cost alternative to Surlyn® and Iotek (Escor®) ionomeric resins in golf ball cover construction while at the same time maintaining properties such as good coefficient of restitution (C.O.R.), softness, as well as the durability required for repetitive play.

These and other objects and features of the invention will be apparent from the following description and from the claims.

SUMMARY OF THE INVENTION

The present invention is directed to golf ball covers, and more particularly to golf ball cover compositions which comprise blends of high or low acid copolymers with ethylene alkyl acrylates. The golf ball covers of the invention provide a desirable low cost alternative to the Surlyn® 15 and lotek ionomeric resins so frequently used in golf ball cover construction when balata is not used.

The present invention is particularly directed to golf ball cover compositions which are prepared by blending an acid copolymer which contains about 1% to about 25% acrylic acid, such as an ethylene acrylic acid (EAA) copolymer, with an ethylene copolymer including up to about 30% by weight of an alkyl acrylate. The alkyl acrylate in the ethylene copolymer may be selected from among ethyl acrylate, methyl acrylate, butyl acrylate, or others. The ethylene copolymer may, therefore, comprise among others ethylene ethyl acrylate (EEA), ethylene methyl acrylate (EMA), and/or ethylene butyl acrylate (EBA). The blending step is followed by the addition of a cation or cation blend for neutralization.

The selection of type and ratio of the ethylene acrylic acid (EAA) copolymer to the ethylene alkyl acrylate (i.e., EEA, EBA, EMA, etc.) is based on the desired final hardness and spin rate of the ball. Preferably, the blend of the acid copolymer with the non-acid functional ethylene alkyl acrylate includes about 30 to 90 parts by weight acid copolymer, and about 10 to 70 parts by weight ethylene alkyl acrylate. More preferably, the blend is comprised of about 40 to 50 parts by weight acid copolymer and about 50 to 60 parts by weight ethylene alkyl acrylate. Most preferably the blend consists of about 50 to about 70 parts by weight acid copolymer and about 30 to 50 parts by weight ethylene alkyl acrylate.

In another aspect, the invention relates to a metal cation neutralized ionomer resin comprising a blend of i) a copolymer of about 1 weight percent to about 25 weight percent, preferably greater than 16 weight percent of an alpha, beta-unsaturated carboxylic acid (preferably acrylic acid) and an olefin (preferably ethylene), and ii) an ethylene alkyl acrylate. Approximately, 10% to about 90% of the carboxyl groups of the acid copolymer are neutralized with a metal cation such as a metal cation selected from the group consisting of manganese, lithium, potassium, calcium, maganese, zinc, sodium, and nickel.

In a further aspect, the present invention concerns a metal cation neutralized high acid ionomer resin comprising a blend of i) a copolymer consisting of about 17 to 25 percent by weight acrylic acid with the remainder, or balance, thereof being ethylene and ii) an ethylene alkyl acrylate. Approximately, 10% to 90% of the carboxyl groups of the acid copolymer are neutralized with a metal cation such as a metal cation selected from the group consisting of manganese, lithium, potassium, zinc, sodium, magnesium, calcium, and nickel.

In another further aspect, the invention relates to a golf ball comprising a core and a cover, wherein the cover is 4

comprised of a blend of i) a copolymer of about 20% by weight of an acrylic acid and the remainder ethylene and ii) an ethylene alkyl acrylate, of which 10% to 90% of the carboxyl groups of the acrylic acid/ethylene copolymer are neutralized with a metal cation such as a metal cation selected from the group consisting of manganese, lithium, potassium, sodium, zinc, magnesium, calcium and nickel. In addition, the cover may contain one or more additional ingredients such as pigments, dyes, U.V. absorbers and optical brighteners. The core is generally a solid core.

Further scope of the applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the development of golf ball covers, and more particularly to golf ball cover compositions which comprise blends of ethylene copolymers (i.e., ethylene alkyl acrylates) with acid copolymers. These blends may be reacted with a neutralizing compound such as magnesium oxide, zinc oxide, zinc acetate, etc. In this regard, a golf ball cover having good durability, playability (spin) and C.O.R. at a low cost relative to Surlyn® or Iotek is provided.

The acid copolymer used herein may contain anywhere from 1 to 25 percent by weight and, it is preferable to utilize a high acid copolymer (i.e. a copolymer containing greater than 16% by weight acid, preferably from about 17 to about 25 weight percent acid, and more preferably about 20 weight percent acid). The acid copolymer is blended with the ethylene alkyl acrylate and the blend is neutralized with a metal cation salt capable of ionizing or neutralizing the copolymer to the extent desired (i.e. from about 10% to 90%).

The base acid copolymer is preferably made up of greater than 16% by weight of an alpha, beta-unsaturated carboxylic acid and an alpha-olefin. Optionally, a softening comonomer can be included in the copolymer. Generally, the alpha-olefin has from 2 to 10 carbon atoms and is preferably ethylene, and the unsaturated carboxylic acid is a carboxylic acid having from about 3 to 8 carbons. Examples of such acids include acrylic acid, methacrylic acid, ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and iraconic acid, with acrylic acid being preferred.

The softening comonomer that can be optionally included in the invention may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms and vinyl ethers wherein the alkyl groups contain 1 to 10 carbon atoms.

Consequently, examples of a number of copolymers suitable for use in the invention include, but are not limited to, high acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight unsaturated carboxylic acid, from about 30 to about 83% by weight ethylene and from 0 to about 40% by weight of a

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softening comonomer. More preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remainder being ethylene.

Along these lines, examples of the preferred high acid base copolymers which fulfill the criteria set forth above, are a series of ethylene-acrylic acid copolymers which are commercially available from The Dow Chemical Company, Midland, Mich., under the "Primacor" designation. These high acid base copolymers exhibit the typical properties set forth below in Table 1.

TABLE 1

	ТТ	ypical Properti	es of Primac	or Ethylene-A	crylic Acid Copo	ymers	
	PERCENT	DENSITY,	MELT INDEX, g/10 min	TENSILE YD, ST (psi)	FLEXURAL MODULUS (psi) ASTM	VICAT SOFT PT (°C.)	SHORE D HARDNESS
GRADE	ACID	D-792	D-1238	D-638	D-790	D-1525	D-2240
5980 5990 5990 5981 5983 5991	20.0 20.0 20.0 20.0 20.0 20.0	0.958 0.955 0.955 0.960 0.958 0.953	300.0 1300.0 1300.0 300.0 500.0 2600.0	 650 650 900 850 635	4800 2600 3200 3200 3100 2600	43 40 40 46 44 38	50 42 42 48 45 40

¹The Melt Index values are obtained according to ASTM D-1238, at 190° C.

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Due to the high molecular weight of the Primacor 5981 ⁴⁰ grade of the ethylene-acrylic acid copolymer, this copolymer is the more preferred grade utilized in the invention.

Other acid copolymers which may be used include an ethylene-methacrylic acid copolymer such as Nucrel® available from E.I. DuPont de Nemours & Co. Nucrel® is an ethylene copolymer which is inherently flexible like EVA copolymers, and which offers desirable performance characteristics similar to those of Surlyn® ionomers.

The Nucrel® acid copolymers are produced by reacting ethylene and methacrylic acid in the presence of free radical initiators. A branched, random ethylene methacrylic acid 55 (EMAA) copolymer is produced thereby. Carboxyl groups are distributed along the chain and interact with carboxyl groups on adjacent molecules to form a weakly crosslinked network through hydrogen bonding. The carboxyl groups 60 disrupt the linearity of the polyethylene.

Nucrel® ethylene copolymers offer tensile strength as high as 25 MPa (3,600 psi) and good performance at low temperatures (945 k J/m² at -40° C.). Properties of selected Nucrel® ethylene copolymers are listed in Table 2.

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TABLE 2

				MICOET & MICOET & MICOET & MICOET & MICOET &							
PROPERTY	UNITS	ASTM	NUCREL ® 010	NUCREL® 035	NUCREL ® 403	NUCREL® 410	NUCREL ® 535				
Melt Index	dg/min	D1238	11	35	3.0	10	35				
Density	g/cm ³	D792	.934	0.94	.934	.933	.934				
Tensile	MPa (kpsi)	D638	22.1	17.9	24.7	21,4	21.4				
Strength			(3.2)	(2.6)	(3.6)	(3.1)	(3.1)				
Elongation	%	D638	630	640	568	600	580				
Flexural	MPa (kpsi)	D790									
Modulus											
23° C.			40.0	59	152	93.8	71				
73° F.)			(5.8)	(8.6)	(22)	(13.6)	(10.3)				
Hardness	Shore D	D2240	40	40	53	49	48				
Vicat	°C,	D1525.	64	60	83	80	75				
Softening	(°F.)	Rate B	(147)	(140)	(181)	(176)	(167)				
Temparature	(*)		(2.11)	(4.0)	,/	47					
Notched Izod	J/m (ft-lb/in)	256	NB1	374 (7)	NB	NB	NB				
Tensile	kJ/m² (ft-lb/in²)	1822S									
Impact	10.111 (11.10.11)										
23° C.			998	1,060	756	872	723				
2(73° F.)			(475)	(505)	(360)	(415)	(344)				
-40° C.			147	945	442	707	486				
(-40° F.)			(308)	(450)	(210)	(336)	(231)				
				(100)	~~~ · · · · · · · · · · · · · · · · · ·	, ,					
			NUCREL ®	NUCREL®	NUCREL ®	NUCREL® 925	NUCREL ®				
					714		960				
PROPERTY	UNITS	ASTM	599	699	734	723	200				
PROPERTY Melt Index		D1238	500	699	14	21	60				
Melt Index	dg/min										
Melt Index Density	dg/min g/cm³	D1238	500 ,918	88	14	21	60				
Melt Index Density Tensile	dg/min	D1238 D792	500 .918 10.3	88 .937 1S.2	14 .937 22.7	21 0.97	60 .941				
Meli Index Density Tensile Strength	dg/min g/cm³	D1238 D792	500 ,918	88 .937	14 .937	21 0.97 25	60 .941 21.4				
Melt Index Density Tensile Strength Elongation	dg/min g/cm³ MPa (kpsi) %	D1238 D792 D638	500 .918 10.3 (1.5)	88 .937 1S.2 (2.2)	14 .937 22.7 (3.3)	21 0.97 25 (3.6)	60 .941 21.4 (3.1)				
Meli Index Density Tensile Strength	dg/min g/cm³ MPa (kpsi)	D1238 D792 D638	500 .918 10.3 (1.5)	88 .937 1S.2 (2.2)	14 .937 22.7 (3.3)	21 0.97 25 (3.6)	60 .941 21.4 (3.1)				
Melt Index Density Tensile Strength Elongation Flexural	dg/min g/cm³ MPa (kpsi) %	D1238 D792 D638	500 .918 10.3 (1.5)	88 .937 1S.2 (2.2)	14 .937 22.7 (3.3)	21 0.97 25 (3.6)	60 .941 21.4 (3.1)				
Melt Index Density Tensile Strength Elongation Flexural Modulus 23° C.	dg/min g/cm³ MPa (kpsi) %	D1238 D792 D638	500 .918 10.3 (1.5) 530	88 .937 18.2 (2.2) \$60	14 .937 22.7 (3.3) 560	21 0.97 25 (3.6) 520	60 .941 21.4 (3.1) 540				
Melt Index Density Tensite Strength Elongation Floxural Modulus 23° C. (73° F.)	dg/min g/cm³ MPa (kpsi) %	D1238 D792 D638	500 .918 10.3 (1.5) 530	88 .937 18.2 (2.2) \$60	14 .937 22.7 (3.3) 560	21 0.97 25 (3.6) 520	50 .941 21.4 (3.1) 540				
Melt Index Density Tensile Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness	dg/min g/cm³ MPa (kpsi) % MPa (kpsi)	D1238 D792 D638 D638 D790	500 .918 10.3 (1.5) 530 64.8 (9.4)	88 .937 18.2 (2.2) \$60 68.3 (9.9)	14 .937 22.7 (3.3) 560 66.9 (9.7)	21 0.97 25 (3.6) 520 74 (10.8)	50 .941 21.4 (3.1) 540 55.1 (8.0)				
Melt Index Density Tensile Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness Vicat	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D	D1238 D792 D638 D638 D790	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65	88 .937 1S.2 (2.2) S60 68.3 (9.9) 46	14 .937 22.7 (3.3) 560 66.9 (9.7) 50	21 0.97 25 (3.6) 520 74 (10.8) 50	60 .941 21.4 (3.1) 540 55.1 (8.0) 46				
Melt Index Density Tensite Strength Elongation Filexural Modulus 23° C. (73° F.) Hardness Vicat Softening	dg/min g/cm³ MPa (kpsi) % MPa (kpsi)	D1238 D792 D638 D638 D790	500 .918 10.3 (1.5) 530 64.8 (9.4)	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74	21 0.97 25 (3.6) 520 74 (10.8) 50 67	50 .941 21.4 (3.1) 540 55.1 (8.0) 46 62				
Melt Index Density Tensite Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness Vicat Softening Temparature	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D °C. (°F.)	D1238 D792 D638 D638 D790	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74	21 0.97 25 (3.6) 520 74 (10.8) 50 67	50 .941 21.4 (3.1) 540 55.1 (8.0) 46 62				
Melt Index Density Tensite Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness Vicat Softening Temparature	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D	D1238 D792 D638 D638 D790 D2240 D1525, Rate B	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65 (149)	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71 (160)	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74 (165)	21 0.97 25 (3.6) 520 74 (10.8) 50 67 (153)	50 .941 21.4 (3.1) 540 55.1 (8.0) 46 62 (144)				
Meh Index Density Tensite Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness Vicat Softening Temperature Notched Izod	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D °C. (°F.)	D1238 D792 D638 D638 D790 D2240 D1525, Rate B	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65 (149)	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71 (160)	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74 (165)	21 0.97 25 (3.6) 520 74 (10.8) 50 67 (153)	50 .941 21.4 (3.1) 540 55.1 (8.0) 46 62 (144)				
Melt Index Density Tensite Strength Elongation Floragation Modulus 23° C. (73° F.) Hardness Vicat Softening Temparature Notched Izod	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D °C. (°F.)	D1238 D792 D638 D638 D790 D2240 D1525, Rate B	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65 (149)	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71 (160)	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74 (165)	21 0.97 25 (3.6) 520 74 (10.8) 50 67 (153)	50 .941 21.4 (3.1) 540 55.1 (8.0) 46 62 (144)				
Melt Index Density Tensile Strength Elongation Fiexural Modulus 23° C. (73° F.) Hardness Vicat Softening Temparature Notched Izod Tensile Impact	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D °C. (°F.)	D1238 D792 D638 D638 D790 D2240 D1525, Rate B	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65 (149) NB	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71 (160)	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74 (165) NB	21 0.97 25 (3.6) 520 74 (10.8) 50 67 (153)	50 .941 21.4 (3.1) 540 55.1 (8.0) 46 62 (144)				
Melt Index Density Tensite Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness Vicat Softening Temparature Notched Izod Tensite Impact 23° C.	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D °C. (°F.)	D1238 D792 D638 D638 D790 D2240 D1525, Rate B	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65 (149) NB	88 .937 1S.2 (2.2) S60 68.3 (9.9) 46 71 (160) NB	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74 (165) NB	21 0.97 25 (3.6) 520 74 (10.8) 50 67 (153) 801 (15)	60 .941 21.4 (3.1) 540 55.1 (8.0) 46 62 (144) NB				
Melt Index Density Tensile Strength Elongation Flexural Modulus 23° C. (73° F.) Hardness	dg/min g/cm³ MPa (kpsi) % MPa (kpsi) Shore D °C. (°F.)	D1238 D792 D638 D638 D790 D2240 D1525, Rate B	500 .918 10.3 (1.5) 530 64.8 (9.4) 42 65 (149) NB	88 .937 18.2 (2.2) \$60 68.3 (9.9) 46 71 (160) NB	14 .937 22.7 (3.3) 560 66.9 (9.7) 50 74 (165) NB	21 0.97 25 (3.6) 520 74 (10.8) 50 67 (153) 801 (15)	60 .941 21.4 (3.1) 540 55.1 (8.0) 46 62 (144) NB				

NB1 = No Break

The cover may comprise about 30-90 percent by weight of an acid copolymer, preferably about 40-80, percent, and most preferably 50-70 percent acid copolymers. At the same time, the cover may comprise about 10-70 percent by weight of an ethylene copolymer, preferably 20-60 percent, 50 and most preferably 30-50 percent ethylene copolymer.

Ethylene copolymers which may be used herein include ethylene-ethyl acrylate (EEA), ethylene-methyl acrylate (EMA), and ethylene-butyl acrylate copolymers. Ethyleneethyl acrylate is made by the polymerization of ethylene 55 units with randomly distributed ethylene acrylate (EA) comonomer groups. The ethylene-ethyl acrylate copolymers contain up to about 30% by weight of ethylene acrylate. They are tough, flexible products having a relatively high molecular weight. They have good flexural fatigue and low 60 temperature properties (down to -65° C.). In addition, EEA resists environmental stress cracking as well as ultraviolet

Examples of ethylene-ethyl acrylate which may be used herein include Bakelite® DPD-6169 or Bakelite® DPD -6182 available from Union Carbide. Properties of these and

other suitable ethylene-ethyl acrylate copolymers include: TABLE 3

TYPICAL PRO	ENE-ETHYL A			
PROPERTY	TEST METHOD	DPD- 6169	DPD- 6182	DPD- 9169
Melt Index, g/10 minutes	D1238	6	1.5	20
Density, g/cm ³	D1505	0.931	0.930	0.931
Flexural Modulus, psi ^(a)	D790	9,500	13,000	9,000
Secant Modulus of	D638	5,000	6,200	4,300
Elasticity, psi ^(a)				
Ultimate Elongation, %(a)	D638	700	700	750
Tensile Strength, psi(a)	D638	1,600	2,100	700
Yield Strength, psi ^(b)	D638	550	700	
Bent Strip Stress Cracking	D1693	>500	<1,000	350
Resistance, 100%				
"Igepai" Solvent, F50,				
hours				

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TABLE 3-continued

TYPICAL PROPERTIES OF UNION CARBIDE ETHYLENE-ETHYL ACRYLATE					
PROPERTY	TEST METHOD	DPD~ 6169	DPD- 6182	DPD- 9169	
Durometer Hardness,	D676				
"A"		88	87	86	
"D"		32	32	31	
Brittleness Index, 50% Failure, °C.	D746	105	66		
Vicat Softening Point, °C.	D1525	64			
Compression Set, 10 days at 23° C., % recovery	D395	56			

⁽a)Determined on 0.075-inch compression molded plaques.

EEA is similar to ethylene vinyl acetate (EVA) in its density-property relationships and high-temperature resistance. In addition, like EVA, EEA is not resistant to aliphatic and aromatic hydrocarbons. For comparison purposes, some typical properties of ionomers as well as ethylene vinyl acetate and ethylene ethyl acrylate are provided below:

TABLE 4

	Iono- mer	EVA	EEA	UNITS
Specific gravity	0.93	0.93~0.95	0.93	
Yield strength	2.2	1.3	1.05	103lbb/in2
Tensil modules	28-40	11	6	10 ³ lbf/in ²
Usual form of fracture	tough	tough	tough	
Vicat softening point	71	83	64	°C.
ASTM	-100	-70	-100	°C.
brittleness temperature				
Power Factor 102 Hz	0.0015	0.0024	0.001	
Dielectric constant 103 Hz	2.5	2.8	2.8	

Ethylene-methyl acrylate copolymers contain up to about 30% by weight of methyl acrylate and yield blown films

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having rubberlike limpness and high impact strength. These copolymers may be useful in coating and laminating applications as a result of their good adhesion to commonly used substrates. EMAs have good heat-seal characteristics.

Ethylene-methyl acrylate copolymers are manufactured by reacting, at high temperatures and pressures, methylacrylate monomers with ethylene and free radical initiators. Polymerization occurs such that the methyl acrylate forms random side chains on the polyethylene backbone. The acrylic functionality decreases resin crystallinity and increases polarity to enhance resin properties. The properties depend on molecular weight (determined by melt index) and percent crystallinity. Percent crystallinity is determined by comonomer incorporation. As the comonomer content increases, the film become softer, tougher, and easier to heat seal.

EMA films have low modulus (<10,000 psi), low melting points, and good impact strength. In addition, the EMA resins are highly polar, and as a result are compatible with olefinic and other polymers. They adhere well to many substrates including LDPE, LLDPE, and EVA.

Examples of ethylene-methyl acrylate which may be used in the golf ball cover compositions of the present invention include the OptemaTM or Escor® EMA copolymer resins available from Exxon Chemical Company. The OptemaTM/ Escor® EMA resins are thermally stable ethylene methyl acrylate resins which will accept up to 65% or more fillers and pigments without losing their properties. They are more thermally stable than EVAs and can be extruded or molded over a range of 275°–625° F. (compared to an EVA limit of 450° F.). EMAs are generally not corrosive when compared to EVAs, EAAs and ionomers. Some of the typical properties associated with the various grades of OptemaTM EMA resins are found in the following Table 5:

TABLE 5

II MANAGE C					
	PROP	erties of opt	ema ® ema resi	NS	
	MELT INDEX dg/min (ASTM D1238)	METHYL ACRYLATE WT %	DENSITY g/cm ³ (ASTM D1505)	TENSILE STRENGTH psi (MPa) (ASTM D638)	FLEXURAL MODULUS psi (MPa) (ASTM D790)
OPTEMA GRADE					
TC 020	6.0	6.5	0.928	1700 (12)	17500 (120)
TC 115	0.7	16.5	0.938	1900 (13)	8300 (57)
TC 114	3.2	18.0	0.948	1700 (12)	7100 (49)
TC 110	2.0	21.5	0.942	1600 (11)	5100 (35)
TC 111	2.0	21.5	0.944	1600 (11)	5100 (35)
TC 120	6.0	20.	0.942	1600 (11)	5100 (35)
TC 130	20.0	21.5	0.941	1300 (9)	4900 (34)
TC 140	135.0	21.5	0.939	1200 (8)	4900 (34)
TC 113	1.0	23.5	0.939	1600 (11)	3700 (26)
TC 220	5.0	24.0	0.945	1300 (9)	3900 (27)
TC 221 DEVELOPMEN- TAL GRADES	5.0	27.0	0.948	1100 (8)	2800 (19)
XS-11.04	6.0	6.0	0.933	1410	11,4000

⁽b) Determined on 0.075-inch compression molded plaques, Material has no true yield point. Value represents tensile strength at 50% elongation.

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TABLE 5-continued

	P	ROPERTIES OF	OPTEMA ® EMA	RESINS	
XS-12.04 XS-13.04	3.0 135.0	28.0 20.	0.953 0.940	(13.3) 760 (5.0) 700 (4.8)	(78.6) 1210 (8.3) 2800 (19)
	MELTING POINT °F. (°C.)	HARDNESS SHORE A/D (ASTM D2240)	TENSILE IMPACT @ 73° F. (23° C.) (ASTM D1822)	ELONGATION % (ASTM D638)	VICAT SOFTENING PT (10,000) (ASTM D1525)
OPTEMA GRADE					
TC 020 TC 115 TC 114 TC 110 TC 111 TC 120 TC 130 TC 140 TC 113 TC 220 TC 221 DEVELOPMENTAL GRADES	215 (102) 185 (85) 178 (81) 167 (75) 167 (75) 169 (76) 167 (75) 162 (72) 165 (74) 156 (69) 147 (64)	>90/45 91/41 89/38 86/36 86/36 86/35 85/33 84/32 83/33 82/32 79/28	170 (360) 260 (550) 260 (570) 270 (570) 270 (570) 250 (520) 230 (480) 170 (360) 310 (650) 280 (580) 280 (590)	>800 >800 >800 >800 >800 >800 >800 >800	172 (78) 149 (65) 133 (56) 126 (52) 126 (52) 117 (47) 109 (43) 97 (36) 122 (50) 109 (43) 102 (39)
XS-11.04 XS-12.04 XS-13.04	225 (107) 145 (63) 171 (77)	90/35 70/17 82/25	170 (363)	1450 1060 1400	182 (84) — 121 (50)

Certain developmental grades of Optema™ EMAs may be used in formulating the golf ball covers herein. These developmental grades of resins are designated "XS". Pertinent properties of XS-11.04, 12.04 and 13.04 are set forth above in Table 5. Melt index and methyl acrylate content of these and certain others are set forth in the following Table

TARLE 6

TABLE 6	40
PROPERTIES OF OPTEMA ® DEVELOPMENTAL EMA RESINS	
	

OPTEMA/GRADE	MELT INDEX (dg/min)	METHYLACRYLATE CONTENT (%)		
XS-53.04	0.7	15		
XS-54.04	. 1.0	24		
XS-34.14*	2.0	20		
XS-12.04	3.0	28		

TABLE 6-continued

PROPERTIES OF OPTEMA ® DEVELOPMENTAL EMA RESINS

OPTEMA/GRADE	MELT INDEX (dg/min)	METHYLACRYLATE CONTENT (%)		
XS-61.48	5.0	24		
XS-55.48	5.0	28		
XS-11.04	6.0	6		
XS-13.04	135.0	20		

^{*}Slip and antiblock added.

Chevron Chemical Company's ethylene-butyl acrylate copolymer, EBACTM, is stable at high temperatures, and may be processed as high as 600° F. Typical properties (or average values) of certain EBACTM copolymers are set forth below in Table 7.

TABLE 7

	PROPERTIES OF ETHYLENE-BUTYL ACRYLATE COPOLYMERS (EBAC ™)						
PROPERTIES	UNITS	ASTM	EBAC TM DS- 1263- 70	EBAC TM DS- 1120- 70	EBAC TM DS- 1122-70	EBAC ™ DS- 1123-70	EBAC TM DS- 1256-70
Melt Flow	gms/10 min	D-1238	0.5	2.0	6.0	20	3.0
Butyl Acrylate Content	%		18	20	20	20	28.0
Density	gm/cc	D-1505	0.927	0.927	0.927	0.927	0.927
Melting Point	°C,		91	90	87	88	74
Vicat Softening	°C.	D-1525	65	60	55	49	*****

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TABLE 7-continued

	PROPERTI	es of eth	YLENE-BUTY	L ACRYLATE	COPOLYME	RS (EBAC™)	
PROPERTIES	UNITS	ASTM	EBAC ™ DS- 1263- 70	EBAC TM DS- 1120- 70	EBAC™ DS- 1122-70	EBAC™ DS- 1123-70	EBAC™ DS- 1256-70
Point Brittleness Temperature Hardness	°C.	D-746	<76	< -7 5	<-75	<-75	<-76
Shore A.	,	D-2240	*****	_	88	88	74
Shore D		D-2240	38	33		27	23
Flexural Stiffness	psi	D-747	4000	***		3000	
Tensile Ultimate ²	psi	D-638	2000	1400	1100	680	760
Tensile @ Break ²	psi	D-638	1900	1400	1100	680	760
Elongation @ Point Break ²	90	D-638	810	900	850	620	950

¹Melt Flow testing of condition E, 190° C. and 2.16 kg weight.

The metal cation salts utilized in the invention are those salts which provide the metal cations capable of neutralizing, to various extents, the carboxylic acid groups of the high acid copolymer. These include acetate, oxide or hydroxide salts of lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese.

Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. Suitable zinc ion sources are zinc acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide, magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

The cover compositions of the invention are produced by reacting the blend of the acid copolymer and the ethylene alkyl acrylate with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a temperature from about 200° F, to about 500° F, preferably from about 250° F, to about 350° F, under high shear conditions at a pressure of from about 100 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the cover compositions is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in the high acid copolymer. The extent of neutralization is generally from about 10% to about 90%.

Additional compatible additive materials may also be added to the compositions of the present invention, such as 60 dyes (for example, Ultramarine Blue sold by Whitaker, Clark, and Daniels of South Painsfield, N.J.), and pigments, i.e. white pigments such as titanium dioxide (for example Unitane 0–110) zinc oxide, and zinc sulfate, as well as fluorescent pigments. As indicated in U.S. Pat. No. 4,884, 65 814, the amount of pigment and/or dye used in conjunction with the polymeric cover composition depends on the par-

ticular base ionomer mixture utilized and the particular pigment and/or dye utilized. The concentration of the pigment in the polymeric cover composition can be from about 1% to about 10% as based on the weight of the base ionomer mixture. A more preferred range is from about 1% to about 5% as based on the weight of the base ionomer mixture. The most preferred range is from about 1% to about 3% as based on the weight of the base ionomer mixture. The most preferred pigment for use in accordance with this invention is titanium dioxide.

Moreover, since these are various hues of white, i.e. blue white, yellow white, etc., trace amounts of blue pigment may be added to the cover stock composition to impart a blue white appearance thereto. However, if different hues of the color white are desired, different pigments can be added to the cover composition at the amounts necessary to produce the color desired.

In addition, it is within the purview of this invention to add to the cover compositions of this invention compatible materials which do not affect the basic novel characteristics of the composition of this invention. Among such materials are antioxidants (i.e. Santonox R), antistatic agents, stabilizers and processing aids. The cover compositions of the present invention may also contain softening agents, such as plasticizers, etc., and reinforcing materials such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers of the invention are not impaired.

Furthermore, optical brighteners, such as those disclosed in U.S. Pat. No. 4,679,795, may also be included in the cover composition of the invention. Examples of suitable optical brighteners which can be used in accordance with this invention are Unitex OB as sold by the Ciba-Geigy Chemical Company, Ardaley, N.Y. Unitex OB is thought to be 2, 5-Bis (5-tert-butyl-2-benzoxazoly) thiophene. Examples of other optical brighteners suitable for use in accordance with this invention are as follows: Leucopure EGM as sold by Sandoz, East Hanover, N.J. 07936. Leucopure EGM is thought to be 7-(2h-naphthol (1,2-d) -triazol-2yl)-3phenyl-coumarin. Phorwhite K-20G2 is sold by Mobay Chemical Corporation, P.O. Box 385, Union Metro Park, Union, N.J. 07083, and is thought to be a pyrazoline derivative, Easto-

²Tensile Properties determined with Type IV compression molded samples, 20"/min crosshead speed.

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brite OB-1 as sold by Eastman Chemical Products, Inc. Kingsport, Tenn., is thought to be 4,4-Bis (-benzoxaczoly) stilbene. The above-mentioned Uvitex and Eastobrite OB-1 are preferred optical brighteners for use in accordance with this invention.

Moreover, since many optical brighteners are colored, the percentage of optical brighteners utilized must not be excessive in order to prevent the optical brightener from functioning as a pigment or dye in its own right.

The percentage of optical brighteners which can be used 10 in accordance with this invention is from about 0.01% to about 0.5% as based on the weight of the polymer used as a cover stock. A more preferred range is from about 0.05% to about 0.25% with the most preferred range from about 0.10% to about 0.020% depending on the optical properties 15 of the particular optical brightener used and the polymeric environment in which it is a part.

Generally, the additives are admixed with a ionomer to be used in the cover composition to provide a masterbatch (M.B.) of desired concentration and an amount of the masterbatch sufficient to provide the desired amounts of additive is then admixed with the copolymer blends.

The cover compositions of the present invention may be produced according to conventional melt blending procedures. In this regard, the above indicated high acid ionomeric resins are blended along with the masterbatch containing the desired additives in a Banbury type mixer, two-roll mill, or extruded prior to molding. The blended composition is then formed into slabs or pellets, etc. and maintained in such a state until molding is desired. Alternatively a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process.

Moreover, golf balls of the present invention can be produced by molding processes currently well known in the 40 golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the novel cover compositions about wound or solid molded cores to produce a golf ball having a diameter of about 1.680 inches or greater and weighing about 1.620 ounces. The standards for both the 45 diameter and weight of the balls are established by the United States Golf Association (U.S.G.A.). Although both solid core and wound cores can be utilized in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound 50 cores.

Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an α , β , ethylenically unsaturated 55 carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include a small amount of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the 60 desired coefficient may be included in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight 65 fatty acids such as stearic acid. Free radical initiator catalysts such as peroxides are admixed with the core composition so

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that on the application of heat and pressure, a complex curing or cross-linking reaction takes place.

The term "solid cores" as used herein refers not only to one piece cores but also to those cores having a separate solid layer beneath the cover and above the core as in U.S. Pat. No. 4,431,193, and other multilayer and/or non-wound cores (such as those described in U.S. Pat. No. 4,848,770).

Wound cores are generally produced by winding a very large elastic thread around a solid or liquid filled balloon center. The elastic thread is wound around the center to produce a finished core of about 1.4 to 1.6 inches in diameter, generally. Since the core material is not an integral part of the present invention, a detailed discussion concerning the specific types of core materials which may be utilized with the cover compositions of the invention are not specifically set forth herein. In this regard, the cover compositions of the invention may be used in conjunction with any standard golf ball core.

As indicated, the golf balls of the present invention may be produced by forming covers consisting of the compositions of the invention around cores by conventional molding processes. For example, in compression molding, the cover composition is formed via injection at about 380° F. to about 450° F. into smooth surfaced hemispherical shells which are then positioned around the core in a dimpled golf ball mold and subjected to compression molding at 200°-300° F, for 2-10 minutes, followed by cooling at 50°-70° F. for 2-10 minutes, to fuse the shells together to form an unitary ball. In addition, the golf balls may be produced by injection molding, wherein the cover composition is injected directly around the core placed in the center of a golf ball mold for a period of time at a mold temperature of from 50° F. to about 100° F. After molding the golf balls produced may undergo various further finishing steps such as buffing, painting, and marking as disclosed in U.S. Pat. No. 4,911,

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight (pbw). It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

EXAMPLES

By blending the ingredients set forth in the Tables below, a series of golf ball cover formulations were produced. Finished golf balls were prepared using the cover compositions of the present invention, controls and comparative cover compositions by positioning a solid preformed crosslinked polybutadiene core in an injection molding cavity in such a manner to permit the uniform injection of the selected cover composition over each core. Along this line, the cover formulations were injection molded at about 400° F. around identical solid type cores having a finished diameter of 1.545 inches to produce golf balls approximately 1.680 inches in diameter having a normal cover thickness of 0.0675 inches. All materials were molded under essentially identical conditions. The properties of coefficient of restitution (C.O.R.) of the molded and finished balls, Shore D hardness, cold crack resistance, spin rates, etc. for the cover compositions were then determined.

In conducting the comparative prior art testing, Escor® 4000/7030 and Escor® 900/8000 ionomers were utilized. In this regard, blends of Escor® 4000/7030 and Escor® 900/ 8000 (i.e. the subject of U.S. Pat. No. No. 4,911,451) are

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considered by the inventors to be generally among the best prior art cover compositions concerning ethylene-acrylic acid ionomer (low acid) blends.

The data for each example represents the average data for one dozen balls produced according to the desired manner.

The properties for the Examples were measured according to the following parameters:

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air cannon at a velocity of 125 feet per second against a steel plate which is positioned 12 feet from the muzzle of the cannon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give the coefficient of restitution.

Shore hardness was measured in accordance with ASTM $_{15}$ Test D-2240.

Cold cracking resistance was measured by firing balls from an air cannon, 5 blows at 165 feet/sec, after the balls had been conditioned for 24 hours at -10° F. After allowing the balls to equilibrate to room temperature the balls are 20 inspected for cover cracking.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9-iron wherein the club-head speed is about 80 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial 25 velocity of about 110–115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

EXAMPLE 1

Preparation of Acrylic Acid Based High Acid Ionomers

A number of new cation neutralized acrylic acid based high acid ionomer resins were prepared utilizing as the 35 copolymer of an olefin and an alpha, beta-unsaturated carboxylic acid, a 20 weight percent acrylic acid/ethylene copolymer produced by The Dow Chemical Company, Midland, Mich, under the designation "Primacor 5981," According to The Dow Chemical Company, Primacor 5981 has a melt index (at 190° C., 2150 g) of 300 g/10 min. The carboxylic acid groups present in the 20 weight percent acrylic acid/ethylene copolymer were neutralized to various weight percentages by a number of different metal cation salts resulting in the production of several new thermoplastic elastomers exhibiting enhanced properties for golf ball cover production. Due to differences in the nature of the cation salts, the amount of cation salts utilized, etc., the new high acid ionomer resins produced differed substantially in the extent of neutralization and in melt indices, as well as in

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resilience (i.e. C.O.R.) and hardness values.

For the purpose of determining the weight percent of neutralization of the carboxylic acid groups in the acrylic acid/ethylene copolymer after reacting with various cation salts, it was assumed that 1 mole of sodium (Na⁺), potassium (K⁺), and lithium (Li⁺) neutralized one mole of acrylic acid, and that one mole of zinc (Zn²⁺), magnesium (Mg²⁺), manganese (Mn²⁺), calcium (Ca²⁺) and nickel (Ni²⁺) neutralized two moles of acrylic acid. The calculations of neutralization were based upon an acrylic acid molecular weight of 79 g/m, giving 0.2778 moles per 100 grams of copolymer.

As indicated below in Table 8, the various cation salts were added in variable amounts to the 20 weight percent acrylic acid/ethylene copolymer in order to determine the optimal level of neutralization for each of the cations. In Table 8, NaOH refers to sodium hydroxide (formula weight of 40). MnAc refers to manganese acetate tetrahydrate having a formula weight of 245. LiOH is lithium hydroxide, fwt=24. KOH is potassium hydroxide, fwt=56. ZnAc is zinc acetate dihydrate, fwt=219.5. MgAc is magnesium acetate tetrahydrate, fwt=214.4. CaAc is calcium acetate, fwt=158. MgO is magnesium oxide, fwt=40.3. NiAc is nickel acetate, fwt=176.8. All of these cation salts are solids at room temperature.

The specific cation salts were added in differing amounts with the 20 weight percent acrylic acid/ethylene copolymer (i.e. the Primacor 5981) to an internal mixer (Banbury type) for the neutralization reaction. The only exception was calcium acetate, which, due to problems encountered in solid form, was added as a 30 wt-% solution in water.

In the neutralization reaction, the cation salts solubilized in the Primacor 5981 acrylic acid/ethylene copolymer above the melting point of the copolymer and a vigorous reaction took place with a great deal of foaming occurring as the cation reacted with the carboxylic acid groups of the acrylic acid/ethylene copolymer and the volatile by-products of water (in the case of oxides or hydroxides) or acetic acid (when acetates are used) were evaporated. The reaction was continued until foaming ceased (i.e. about 30-45 minutes at 250°-350+F.), and the batch was removed from the Banbury mixer. Mixing continued of the batch obtained from the mixer on a hot two-roll mill (175°-250° F.) to complete the neutralization reaction. The extent of the reaction was monitored by measuring melt flow index according to ASTM D-1238-E. As indicated below, the neutralized products exhibited drastically different properties depending upon the nature and amount of the cation salts utilized.

TABLE 8

	IADLC 0						
Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness		
l (NaOH)	6,98	67.5	0.9	.804	71		
2 (NaOH)	5.66	54,0	2.4	.808	73		
3 (NaOH)	3.84	35.9	12.2	.812	69		
4 (NaOH)	2.91	27.0	17.5	.812	(brittle)		
5 (MnAc)	19.6	71.7	7.5	.809	73		
6 (MnAc)	23.1	88.3	3.5	.814	77		
7 (MnAc)	15,3	53.0	7.5	.810	72		
8 (MnAc)	26.5	106	0.7	.813	(brittle)		
9 (LiOH)	4.54	71.3	0,6	.810	74		
10 (LiOH)	3.38	52.5	4.2	.818	72		
11 (LiOH)	2.34	35.9	18.6	.815	72		
12 (KOH)	5 30	36.0	193	Broke	70		

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TABLE 8-continued

Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness
13 (KOH)	8.26	57.9	7.18	.804	70
14 (KOH)	10.7	77.0	4.3	.801	67
15 (ZnAc)	17.9	71.5	0,2	.806	71
16 (ZnAc)	13.9	53.0	0.9	.797	69
17 (ZnAc)	9.91	36.1	3.4	.793	67
18 (MgAc)	17.4	70.7	2.8	.814	74
19 (MgAc)	20.6	87.1	1.5	.815	76
20 (MgAc)	13.8	53,8	4.1	.814	74
21 (CaAc)	13.2	69.2	1.1	.813	74
22 (CaAc)	7.12	34.9	10.1	.808	70
23 (MgO)	2.91	53.5	2.5	.813	
24 (MgO)	3.85	71.5	2.8	.808	
25 (MgO)	4.76	89.3	1,1	.809	
26 (MgO)	1.96	35.7	7,5	.815	
27 (NiAc)	13.04	61.1	0.2	.802	71
28 (NiAc)	10.71	48.9	0.5	.799	72
29 (NiAc)	8.26	36.7	1.8	.796	69
30 (NiAc)	5.66	24.4	7.5	.786	64

Controls:

50/50 Blend of Ioteks 8000/7030 C.O.R. = 810/65 Shore D Hardness DuPont High Acid Surlyn ® 8422 (Na) C.O.R. = 811/70 Shore D Hardness DuPont High Acid Surlyn ® 8162 (Zn) C.O.R. = 807/65 Shore D Hardness Exxon High Acid Iotek EX-960 (Zn) C.O.R. = 796/65 Shore D Hardness

Control for Formulations 23-26 is 50/50 lotek 8000/7030, C.O.R. = .814, Formulation 26 C.O.R.

was normalized to that control accordingly Control for Formulation Nos. 27-30 is 50/50 Iotek 8000/7030, C.O.R. = .807

As indicated in Table 8, a number of the new cation neutralized acrylic acid based high acid ionomer resins 30 exhibited C.O.R. and Shore D hardness values greater than that exhibited by a 50/50 blend of the lotek low acid acrylic acid based hard ionomer resins, such as the Totek 8000/7030 blend utilized in the cover compositions disclosed in U.S. Pat. No. 4,911,451. Moreover, included in new acrylic acid 35 based high acid ionomer resins were numerous cation neutralized high acid ionomer resins previously not available, such as those acrylic acid based high acid ionomer resins neutralized to various degrees by the manganese, lithium, potassium, magnesium, calcium and nickel salts. Furthermore, the new cation neutralized acrylic acid based high acid ionomers produced C.O.R. and hardness values greater than those shown by the methacrylic acid based high acid ionomer resins recently produced by DuPont (i.e. Surlyn® 8422 (Na) and Surlyn® 8162 (Zn)) and the acrylic acid based high 45 acid resins experimentally produced by Exxon (i.e. Iotek EX-959 and Ex-960 (Zn)), collectively referred to as "the controls."

In addition, the results produced by Formulation Nos. 1 through 3 directed to the sodium ion neutralized ethylene- 50 acrylic acid copolymers and Formulation Nos. 15 through 17 directed to the zinc ion neutralized ethylene/acrylic acid copolymers in comparison to the new lotek high acid ethylene acrylic acid ionomers were also of interest. As indicated above, Escor® or Iotek Ex-959 is a sodium ion 55 neutralized ethylene-acrylic acid copolymer and Escor® or Iotek Ex-960 is a zinc neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups 60 neutralized with sodium and zinc ions, respectfully.

Formulation No. 2 (i.e. 5.66 wt-% sodium salt, 54 wt-% neutralization, 2.4 melt index, 0.808 C.O.R. and 73 Shore D hardness) is somewhat similar to Iotek 959 and Formulation No. 16 (i.e. 13.9 wt-% zinc salt, 53 wt-% neutralization, 0.9 65 melt index, 0.797 C.O.R. and 69 Shore D hardness) is somewhat similar to Iotek 960.

However, not only did the new cation neutralized acrylic acid based high acid ionomers exhibit similar or better resilience (C.O.R.) at comparable or better hardness values than those exhibited by the sodium or zinc high acid lotek ionomers, as a result of the neutralization of the acrylic acid/ethylene copolymer with several different cation salts, to a number of different neutralization percentages, a wide variety of new cation neutralized acrylic acid based high acid ionomers were produced having improved resilience and hardness values. These new cation neutralized high acid ionomer resins are particularly valuable in the field of golf ball production.

More particularly, the development of a number of separate different cation neutralized high acid ionomers besides the sodium or zinc high acid ionomers available from DuPont or Exxon, such as the new manganese, lithium, potassium, magnesium, calcium and nickel acrylic acid based high acid ionomer resins, allows for the production of a wide variety of cation neutralized high acid ionomer blends. Furthermore, since the new sodium or zinc neutralized high acid ionomers produced improved properties over those produced by the existing available sodium or zinc high acid ionomers, a number of new cover compositions can be produced having enhanced characteristics.

Along this line, several of the cation neutralized acrylic acid based high acid ionomer resins produced above which exhibited enhanced C.O.R. and Shore D hardness values were blended together and evaluated for the purpose of determining whether any synergistic effects were produced particularly with respect to enhanced C.O.R. values.

Specifically, from each group of the different cation neutralized high acid ionomer resins set forth in Table 8, the best overall ionomer (based upon C.O.R., melt index and Shore D hardness) was utilized to produce a number of blends ("diblends" and "triblends") and processed to produce the cover component of multi-layered golf balls. The "diblends" consisted of 50/50 mixtures and the "triblends" consisted of a 33.33/33.33/33.33 mixtures.

With respect to the blends set forth below, Na refers to Formulation No. 3, C.O.R. (molded/finished) of 0.812/817;

Mn refers to Formulation No. 6, C.O.R. (molded/finished) of 0.814/0.814; Li refers to Formulation No. 10, C.O.R. (molded/finished) of 0.818/0.819; K refers to Formulation No. 13, C.O.R. (molded/finished) of 0.805/0.809; Zn refers to Formulation No. 16, C.O.R. (molded/finished) of 0.797/ 5 0.796; Mg refers to Formulation No. 18, C.O.R. (molded/finished) of 0.814/0.820; Ca refers to Formulation No. 21, C.O.R. (molded/finished) of 0.814/0.820; Ca refers to Formulation No. 28, C.O.R. (molded/finished) of 0.799/0.817; and 50/50 lotek 8000/7030 refers to control of 50/50 blend 10 of lotek 8000/7030, C.O.R. (molded/finished) of 0.810/ 0.812. The C.O.R. values of the "diblends" and "triblends" were then evaluated after molding with a center stock having the following composition:

MATERIAL	WEIGHT (plr)	
BR-12201	70.70	
Taktene 220 ²	29.30	
React Rite ZDA ³	31.14	20
Zinc Oxide	6.23	20
Zinc Stearate	20.15	
Limestone	17.58	
Ground Flash (20-40 mesh)	20.15	
Blue Masterbatch	.012	
Luperco 231XL ⁴	.89	
or Trigonox 29/405		25
Papi 94 ⁶	<i>_</i> 50	

¹BR-1220 is high cis-polybutadiene from Shell Chemical Co., Houston Texas. ²Taktene is high cis-polybutadiene from Polysar Chemical.

Midland, Michigan.

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TABLE 9A

	Diblends (50/	50 Blends) C.O.R. ((Molded/Finished) Values
5	Fermulation No.	Blend	C.O.R. (Molded/Finished)
	31	Na/Mn	.813/.818
	32	Na/Li	.813/.818
	33	Na/K	.809/.816
	34	Na/Zn	.811/.818
10	35	Na/Mg	.813/.819
	36	Na/Ca	.811/.819
	37	Mn/Li	.811/.817
	38	Mn/K	.811/.818
	39	Mn/Zn	.807/.814
	40	Mn∕Mg	.809/.816
15	41	Mn/Ca	.809/.816
13	42	Li/K	.810/.817
	43	Li/Zn	.813/.819
	44	Li/Mg	.812/.820
	45	Li/Ca	.811/.818
	46	K/Zn	.810/.815
	47	K/Mg	.811/.820
20	48	K/Ca	.810/.817
	49	Zn/Mg	.807/,814
	50	Zn/Ca	.808/.814
	51	Mg/Ca	.801/.818
	52	Na/Ni	.809/.815
	53	Mn/Ni	.807/.814
25	54	Li/Ni	.809/.816
	55	K/Ni	.809/.816
	56	Zu/Ni	.799/.804
	57	Mg/Ni	.805/.813
	58	Ca/Ni	.807/.815
	59	Iotek 959/960	.811/.818
30	60	Control	.809/NA
,,,,	6I.	Control	.806/NA

Controls are Formulation No. 59, a 50/50 blend of Iotek 959/960; Formulation No. 60 a 75/25 blend of Surlyn 8162/8422; and Formulation No. 61 a 50/50 blend of Iotek 8000/7030.

TABLE 9B

			S	ynergy Va	dues of the Dil	Blends		
Formulation No.	Salt 1	Salt 2	(COR)	(COR)	(COR) exp – (COR) calc	Final (COR) calc	Final (COR) exp	Final (COR) Diff
31	Na	Mn	813.0	813.0	0.0	815.5	818.0	2.5
32	Na	Li	815,0	813.0	-2.0	818.0	818.0	0.0
33	Na	K	808.0	809.0	1.0	813.0	816.0	3.0
34	Na	Zα	804.5	811,0	6.5	806.5	818.0	11.5
35	Na	mg	813.0	813.0	0.0	818.5	819.0	0.5
36	Na	Ca	812.5	811.0	-1.5	814.5	819.0	4.5
37	Mn	Li	816.0	811.0	5.0	816.5	817.0	0.5
38	Mn	K	809.0	811.0	2.0	811.5	818.0	6.5
39	Mn	Zn	805.5	807.0	1.5	805.0	614.0	9.0
40	Мn	Mg	814.0	809.0	-5.0	817.0	816.0	-1.0
41	Mn	Ca	813.5	809.0	-4.5	813.0	816.0	3.0
42	Li	K	811.0	810.0	1.0	814.0	817.0	3.0
43	Lá	Zn	807.5	813.0	5.5	807.5	819.0	11.5
44	Li	Mg	816.0	812.0	-4.0	819.5	820,0	0.5
45	Li	Ca	815.5	811.0	-4.5	815.5	818.0	2.5
46	ĸ	Zn	800.5	810.0	9.5	802.5	815.0	12.5
47	ĸ	Mg	809.0	811.0	2.0	814.5	820.0	5.5
48	K	Ca	806.0	810.0	4.0	810.5	817.0	6.5
49	Zn	Mg	805.5	807.0	1.5	808.0	814.0	6.0

³ZDA is zinc diacrylate.

⁴Luperco 231XL is a peroxide-free radical initiator manufactured and sold by Atochem, Buffalo, New York.

Trigonox 29/40 is peroxide-free radical initiator manufactured and sold by

Ingonox 2940 is peroxice-ree ranca initiator manufactured and soft by Akzo Chemie America, Chicago, Illinois. ⁶Papi 94 is a polymeric diisocyanate available from Dow Chemical Co.,

In addition, the molded balls were coated and finished according to the procedure mentioned above. The C.O.R. values of the finished balls were determined in order to evaluate whether any improvement in resilience was produced. Generally, it is typical to observe a 0.002 to 0.003 point pick up in C.O.R. values of the finished balls in comparison to the molded balls. The results are set forth in Tables 9A, 9B and 10 below.

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TABLE 9B-continued

1			s	ynergy Va	dues of the Di	Blends		
Formulation No.	Salt 1	Salt 2	(COR)	(COR)	(COR) exp - (COR) calc	Final (COR) calc	Final (COR) exp	Final (COR) Diff.
50	Zn	Ca	805.0	808.0	3.0	804.0	814.0	10,0
51	Mg	Ca	813.5	810.0	-3.5	816.0	818.0	2.0
52	Na	Ni	805.5	809.0	3.5	817.0	815.0	2.0
53	Mn	Ni	806.5	807.0	0.5	815.5	814.0	1.5
54	Li	Ni	808.5	809.0	0.5	818.0	816.0	-2.0
55	K	Ni	801.5	809.0	7.5	813.0	816.0	3.0
56	Zn	Ni	798.0	799.0	1.0	806.5	804.0	~2.5
57	Mg	Ni	806.5	805.0	1.5	818.5	813.0	-5.5
58	Ca	Ni	806.0	807.0	1.0	814.5	815.0	0.5

In Table 9B above, the C.O.R. synergy values are based upon the data from Table 8 of the various metal cation neutralized high acid acrylic acid based ionomer resins and 20 the following calculations:

(COR) calc=coefficient calculated as weighted average of as-molded COR's for polymers of salts 1 and 2

(COR) exp=experimental as-molded COR for blend FINAL (COR) calc=coefficient calculated as weighted average of finished COR's for polymers of salts 1 and 2

FINAL (COR) exp=experimental finished COR for blend FINAL (COR) diff=difference between FINAL (COR) 30 exp and FINAL (COR) (calc)

As noted in Table 9B, positive synergy in resilience is observed for nearly all of the finished (final) blends, with substantial synergy being produced in Formulation Nos. 34, 38, 39, 43, 46, 48, 49, 50.

Moreover, the diblends were also evaluated against a control Formulation No. 59 (see Table 9A), a 50/50 blend of Iotek 959/960, the best available high acid blends, with respect to improved C.O.R. values (i.e. 811/0.818). Similar or enhanced C.O.R. values (molded/finished) were observed in Formulation Nos. 31 (Na/Mn), 32 (Na/Li), 34 (Na/Zn), 35 (Na/Mg), 36 (Na/Ca), 38 (Mn/K), 43 (Li/Zn), 44 (Li/Mg), 45 (Li/Ca), and 47 (K/Mg).

Furthermore, when reviewed for cold cracking, with the exception of Formulation No. 35, all of the diblends tested exhibited resistance to breaking. With respect to Formulation No. 35, some breakage did occur with 2 out of the 12 balls tested exhibiting breakage.

When the small test sample of the triblends were evaluated (see Table 10 below) in comparison to a 50/50 blends of the low acid acrylic acid based hard ionomers (i.e. Iotek 8000/7030 U.S. Pat. No. 4,911,451), all of the cation neutralized high acid acrylic acid based triblends produced 55 enhanced C.O.R. values upon molding and finishing. In addition, when subjected to cold cracking, no breakages were observed.

TABLE 10

Formulation	Cation Blend	C.O.R. Molded	C.O.R. Finished Ball
62	Zn/Li/K	.819	.828
63	Na/Zn/Li	.821	.829
64	Iotek 8000/7030	.816	.819
65	Na/Mn/Ca	.820	.828
66	Na/K/Mn	.821	.829
67	Na/K/Mg	.821	.829

Consequently, not only are a number of new cation neutralized acrylic acid based high acid ionomers now available for golf ball cover construction, these new cation neutralized acrylic acid based high acid ionomers may be blended together in various combinations to produce cover compositions exhibiting enhanced resilience (i.e. distance) due to the synergies noted above.

EXAMPLE 2

In order to determine whether the diblends or triblends of the new cation neutralized acrylic acid based high acid ionomer resins produced different results when dry blended (i.e. prepared as simple dry blends of pre-made single cation neutralized acrylic acid based high acid ionomers, such as those set forth in Example 1 above) or when produced as "in-situ" cation blends (i.e. the cations were first blended and then added to the acrylic acid/ethylene copolymers in the Banbury mixer), a number of comparison reactions were generated. Specifically, in-situ Formulation Nos. 68–72 in Table 11 below correspond to dry-blended Formulation Nos. 31, 32, 43, 44 and 46, respectively, and in-situ Formulation Nos. 73 and 74 in Table 11 below correspond to dry-blended Formulation Nos. 62 and 63, respectively.

TABLE 11

Formulation No.	Cation Blend	C.O.R Molded	C.O.R. Finished	Spin Rate 9-Iron, RPM	Shore D Hardness
68	Na/Mn	.822	.828	5,008	74
69	Na/Li	.820	.828	5,820	70

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TABLE 11-continued

Formulation No.	Cation Blend	C.O.R Molded	C.O.R. Finished	Spin Rate 9-Iron, RPM	Shore D Hardness
70	Li/Zn	.820	.825	5,425	71
71	Lì/Mg	.821	.828	5,451	73
72	Zn/K	.817	.821	5.934	69
73	Li/Zn/K	.822	.826	5,266	71
74	Na/Li/Zn	.821	.824	5,165	71
75	Iotek 959(Na)/960(Zn)	.819	.824	5,926	
Tour Edition ® 100	. , , ,			10,124	
Tour Edition ® 90				9,821	
Top-Flite ® XL II				6,942	

The results indicated that little difference in C.O.R. was produced (relative to a control of 50/50 mixture of the high acid Iotek 959/960) whether a dry blending process or an in-situ blending process was used. Moreover, the data further clearly indicated that the cation neutralized acrylic acid 20 based high acid ionomer blends of the present invention generally exhibit higher C.O.R. values and significantly generally exhibit higher C.O.K. values and significantly lower spin rates than the best acrylic acid based high acid ionomers (i.e. the Ioteks 959(Na)/960(Zn) blend), see Formulation Nos. 68, 70, 71, 73 and 74 in comparison to Formulation No. 75 (control). The lower C.O.R. value and 25 the substantially similar spin rate produced by the Zn/K blend in Formulation 72 was attributed to the slightly lower hardness of this blend versus the others. As indicated in Table 8, the K and Zn acrylic acid based high acid ionomers are a little softer than the Na, Mn, Li and Mg acrylic acid based high acid ionomers. Similarly, the higher spin rate of the Na/Li blend in Formulation 69 was due to its relative softness versus the other blends. In addition, other more subtle factors may also be at play, such as differences in coefficient of friction, deformation under load, etc., which have not quantified.

In addition, when compared with a number of commercially available balls produced by Spalding & Evenflo Companies, Inc., the assignee of the present invention, with low acid ionomer resin covers (i.e. the Tour Edition® 100, Tour Edition® 90 and Top-Flite® XL II balls), the spin rates

neutralized acrylic acid based high acid ionomer blends of the present invention produced, when utilized to formulate the cover of a multi-layered golf ball, a much harder surface then those produced by the low acid ionomer covers presently available. This may be desirable to a golfer who imparts unmanageable spin (slice/hook) to the ball and therefore may benefit from a "low spin" ball.

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EXAMPLE 3

Acrylic Acid Based High Acid Ionomer Di-Blends Containing Varying Ratios of Cation Neutralized Acrylic Acid Based High Acid Ionomers

In addition to the 50/50 blends of various combinations of the new cation neutralized acrylic acid based high acid ionomers set forth in Example 1, di-blends varying from 25/75 to 75/25 ratios were produced utilizing the more preferred diblends in the "in-situ" process described in Example 2. In this regard, the more preferred diblend formulations set forth in Example 1 (i.e. Formulation No. 31 (Na/Mn), Formulation No. 32 (Na/Li), Formulation 43 (Li/Zn), Formulation No. 44 (Li/Mg), and Formulation No. 46 (Zn/K)) were produced in-situ in 50/50, 25/75 and 75/25 combinations according to the following formulations:

TABLE 12

					Form	nulation	iS			
Ingredients	76	77	78	79	80	81	82	83	84	85
Acid Copolymer (Primacor 5981)	100	100	100	100	100	100	100	100	100	100
NaOH	2.0	1.0	3.0	2.0	1.0	3.0				
Mn Acetate	15.0	22.5	7.5							
Lithium Hydroxide Monohydrate	_		Nontrie	3.1	4.7	1.6	3.1	1.6	4.7	3.1
Zinc Acetate			-			h-4	8.00	12.0	4.0	
Potassium Hydroxide			-			-		_		-
Magnesium Acetate		****					-			10.5
						Formul	ation N	0.	~~~~~	
Ingredients		1	86	. 87		88	. 8	39	90	
Primacor 5981			100	10	0	100		100	100)
Lithium Hydroxi	de		1.6	4.7	,		-			
Magnesium Acet	ate		15.8	5.3	1	_	-			
Zinc Acetate						8.00	1	12.0	4.0	+
Potassium Hydro	oxide					4.50	2	2.25	6.7	5

of the cation neutralized acrylic acid high acid ionomer 65 blends of the present invention (i.e. Formulations 68-75) exhibited much lower spin rates. Consequently, the cation

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The di -blends produced the following C.O.R. values:

TABLE 13

Formulation No.	Cation Blend	C.O.R. (Molded)
76	50/50 Na/Mn	.820
77	25/75 Na/Mn	.821
78	75/25 Na/Mn	.825
79	50/50 Na/Li	.822
80	25/75 Na/Li	.822
81	75/25 Na/Li	.823
82	50/50 Li/Zn	.816
83	25/75 Li/Zn	.804
84	75/25 Li/Zn	.825
85	50/50 Li/Mg	.823
86	25/75 Li/Mg	.822
87	75/25 Li/Mg	.821
88	50/50 Zn/K	.820
89	75/25 Zn/K	.798
90	25/75 Zu/K	.821

Control is a 50/50 lotek Low Acid Ionomer Blend (8000/7030), C.O.R. (molded) .817

The results indicated that in general the new cation neutralized acrylic acid based high acid ionomer diblends produced enhanced C.O.R. values over the known acrylic acid based low acid ionomer blends. See Formulation Nos. 76–81, 84–88 and 90. While Formulation 82 produced a 25 lower C.O.R. value than expected, the data suggested that in some cases, a 50/50 blend is not optimal (particularly in the Zn/K and the Li/Zn blends), while in others (i.e. Li/Mg, Na/Li) the blend ratio is not significantly different.

EXAMPLE 4

Since the data set forth in Examples 1–3 indicated the resilience (C.O.R.) and/or hardness properties of the cover compositions can be substantially enhanced through the use of the new cation neutralized acrylic acid based high acid ionomers and/or diblends or triblends of such ionomers, the molecular weight property of the acrylic acid/ethylene copolymers utilized to produce the ionomers was evaluated. Specifically, the molecular weight of the acid copolymers was assessed for the purpose of determining whether further enhanced properties can be produced by varying the molecular weight of the acid copolymer.

In this regard, since the data indicated that there was little difference between using the dry blending process or the in situ blending method for processing the cations, the in-situ method of producing the cation neutralized high acid ionomer blends was used in this analysis.

Along this line, the diblend and triblends set forth in Formulation Nos. 68, 73 and 74 are essentially the same as those set forth below in Formulation Nos. 91, 94 and 97, respectively. However, since a different batch of cores was utilized than those used in Example 2, the C.O.R.'s are slightly lower. While the cores utilized in the present Example were of the same composition, the lower C.O.R.

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was due to the age of the cores, i.e. molded cores will lose C.O.R. upon aging mainly due to moisture pickup. Formulation Nos. 92-93, 95-96 and 98-99, are similar to those set forth in Formulation Nos. 91, 94 and 97, respectively, with the exception that the molecular weight of the acrylic acid/ethylene copolymer utilized was varied. Specifically, Primacor 5983 and Primacor 5990 both contain the same acid content as Primacor 5981 (i.e. 20 weight percent acrylic acid) but have lower viscosities (lower molecular weights) and lower densities. Primacor 5981 has a melt index of 300 g/10 minute (ASTM Method D-1238 at 190° C.) and a Brookfield viscosity of 51,000 cps at 350° F. Primacor 5983 has a melt index of 500 and a Brookfield viscosity of 26,000 cps at 350° F.; and Primacor 5990 has a melt index of 1300 15 and viscosity of 13,000 cps at 350° F.

The resilience (C.O.R.) of the molded balls produced utilizing the different molecular weight acrylic acid/ethylene copolymers are set forth below in Table 14.

TABLE 14

Formulation No.	Cations	Acid Copolymer	C.O.R. (MOLDED)
140.	Cauons	Сорогупис	(1100000)
91	Na/Mn	Primacor 5981	.813
92	Na/Mn	Primacor 5983	.805
93	Na/Mn	Primacor 5990	All Balls crack
94	Li/Zn/K	Primacor 5981	.814
95	Li/Zn/K	Primacor 5983	809
96	Li/Zn/K	Primacor 5990	All Balls crack
97	Na/Li/Zn	Primacor 5981	.813
98	Na/Li/Zo	Primacor 5983	808
99	Na/Li/Zn	Primacor 5990	All Balls crack

The data indicated that a higher molecular weight acid copolymer is preferred for obtaining high resilience (i.e. C.O.R.) and required toughness.

EXAMPLE 5

By way of further example, golf ball cover compositions were prepared by first blending an acid copolymer such as ethylene acrylic acid copolymer (EAA) with a non-acid functional polymer such as ethylene-ethyl acrylate (EEA) and/or ethylene-methyl acrylate (EMA). This was followed by addition of a cation or cation blend for neutralization. Selection of the type and ratio of acid copolymer to EEA or EMA was based upon the desired final properties of the ball such as hardness or spin rate. Tables 15–17 show the compositions and properties of balls having covers prepared using ethylene acrylates, and Table 18 shows the properties of several golf balls produced by the present assignee which do not contain ethylene acrylates but exhibit somewhat similar properties.

Table 15 below provides for the results of simple blends of ionomers with various non-acid functional polymers. Iotek's 959 and 960 were selected for their similarity in properties to ionomers made from Primacor 5981.

TABLE 15

IABLE 13								
Formulation No.	100	101	102	103	104	105	106	107
Iotek 959	50	25	25	25	25	25	25	25
lotek 960	50	25	25	25	25	25	25	25
Kraton FG-1901X		50					*****	
EEA 6169			50					
EEA 6182	******	*****	_	50	-		-	-
EMA 53.04		*****	_		50			
EMA XS 12 04						50		

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TABLE 15-continued

Formulation No.	100	101	102	103	104	105	106	107
EMA TC-130					,		50	,
Fusabond D-197			-				****	50
Compression	56	59	61	60	61	61	63	60
Molded COR	.818	.797*	.797	.798	.797	.798	.793*	.796
Finished COR	.821	.798	.795	.798	.797	.799	.787	.796
Shore C Hardness	98	85	86	88	80	85	80	88
Cut Resistance	45	3	2-3	2	2	2	2	2
Spin Rate (full 9 iron)	5,969	9,495	8,997	9,260	9,145	9,732	9,857	9,340

^{*}Several balls cracked on Formulations 101 and 106 during COR testing.

Blends similar to those of Table 15 were prepared using Primacor 5981 as the acid copolymer of choice instead of lotek 959/960. These blends, and the resulting properties, are set forth below in Table 16: One of the objectives in preparing the formulations listed in Tables 15–17 was to make a soft covered golfball having properties similar to the current "Tour" balls of the present assignee. The properties of the subject assignee's Titleist

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TABLE 16

108	109	110	111	112	113	114	115
100	50	50	50	50	50	50	50
*****				-			-
erentmer.	50			_	******	-	
	*****	50		_			
			50			•	*****
****				50			
****					50		
		Named .				50	
*****		****	******	-		****	50
5.33	5.33	5.33	5.33	5,33	5.33	5.33	5.33
3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05
55	62	60	60	63	63	62	62
.820	.802	.792	.794	.791	.790	.793	.802
.825	.802	.792	.796	.793	.790	.794	.801
98	90	86	90				88
45	3	3	3	2	_		3-4
5,787	8,834	9,232	9,148	10,220	9,516	9,552	9,091
	100 5.33 3.00 2.05 55 .820 .825 98 4-5	100 50 50 50 50 50 533	100 50 50 50 50 50 50 50 50 50 50 50 50 5	100 50 50 50 50 50 50 50 50 50 50 50 50 5	100 50 50 50 50 50	100 50 50 50 50 50 50 50 50 50 50 50 50 5	100 50 50 50 50 50 50 50 50 50 50 50 50 5

While Primacor 5981 has been the acid copolymer of 40 choice herein as a result of its high COR, it should be noted that lower acid copolymers or a blend of acid copolymers may be used with satisfactory results. Table 17 below shows several compositions using lower acid copolymers or a blend of acid copolymers, along with the resulting properties of the finished cover and ball.

TABLE 17

	TLITIT	AL				
Formulation No.	116	117	118	119	120	50
Primacor 5981		·		25	-	
Nucrel 960	50	50	50	25	100	
Kraton FG-1901X						
EEA 6169	_	_			-	
EEA 6182	50		*****			55
EMA 53.04		50	*****	50		
EMA X512.04						
EMA TC-130						
Fusabond D-197		herman	50		_	
Zinc Acetate	4.00	4.00	4.00	4.70	4.00	
Potassium Hydroxide	2.27	2.27	2.27	2.60	2.27	60
Lithium Hydroxide	1.50	1.50	1.50	1.80	1.50	
Compression	68	66	64	64	58	
Molded COR	.793	.789	.800	.790	.813	
Finished COR	.793	.788	.798	.790	.815	
Shore C Hardness	86	75	88	76	96	
Cut Resistance	3	3	3	3	4	65
Spin Rate (Full 9 Iron)	9,436	10,306	9,315	10,168	7,014	

Tour 100, Tour Edition 100, Tour Edition 90, and Top-Flite XL II are provided in Table 18. These properties may be compared with those listed in Tables 15–17 to find many similarities such that a lower cost alternative may be provided.

TABLE 18

	Titleist Tour 100	Tour Edition 100	Tour Edition 90	Top- Flite XL II
Compression	[.] 75	57	55	47
Molded COR				*****
Finished COR	.786	.809	.813	.814
Shore C Hardness	82	84	86	96
Cut Resistance	1	3	3	4-5
Spin Rate (Full 9 Iron)	9,422	9,924	9,703	6,968

Little is known of the reaction mechanism or to what extent the EEA and/or EMA actually take part in the reaction of EEA/EMA with an acid copolymer and the addition of a cation or cation blend for neutralization. There is, however, some belief that there is at least enough interaction between polymers to provide a net benefit in properties versus a simple blend of an ionomer and EEA/EMA. It is possible that an interpenetrating polymer network (IPN) is formed by reacting (neutralizing) the acid copolymer in the presence of EEA/EMA. By first forming an intimate blend of polymers and then neutralizing one in the presence of another it is

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possible that a network is formed via intermolecular chain entanglement of the two polymers.

It is also possible that a dynamic vulcanization takes place where superior properties are the result of a finer phase morphology of the dispersed crosslinked phase (here, the neutralized acid copolymer) in an essentially uncrosslinked continuous matrix of ethylene acrylate ester.

The formations of Tables 15–17 above include examples of an acid copolymer reacted in the presence of maleic anhydride functional elastomers Kraton FG-1901X and Fusabond D-197. In simple blends with ionomers, this was the subject of U.S. Pat. Nos. 4,986,545 and 5,098,105, incorporated herein by reference.

A further advantage of the reactive blends of Tables 16 and 17 over the non-reactive blends of Table 15 is the improved cut resistance. While most of the blends of Table 15 give an undesirable "2" rating, nearly all of those in Tables 16 and 17 give a rating of "3", which is comparable to the current Tour balls (see, e.g. Table 18). It should be further noted that formulations 101 and 106 in Table 15 had several balls break during COR testing. The related formulations in Table 16 (formulations 109 and 114) did not have this problem. In general, although no COR advantage is observed (i.e., some COR values of Table 16 are higher and some are lower than the corresponding Table 15 formulations) the balls prepared using the formulations of Table 16

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are tougher, slightly softer and more durable than those of Table 15.

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon a reading and understanding of the preceding detailed description. It is intended that the invention be construed as including all such alterations and modifications insofar as they come within the scope of the appended claims or the equivalents thereof.

We claim:

- 1. A golf ball having a core and a cover wherein said cover comprises:
 - (a) about 30 to 90 parts by weight of a copolymer of an olefin and about 16% to about 25% by weight of an alpha, beta unsaturated carboxylic acid partially neutralized with a metal cation, and (b) about 10 to 70 parts by weight of an ethylene/alkyl acrylate copolymer having up to about 30% by weight of an alkyl acrylate.
- 2. A golf ball having a core and a cover wherein said cover comprises:
 - (a) about 30 to 90 parts by weight of a copolymer of an olefin and about 20% by weight acrylic acid partially neutralized with a metal cation, and (b) about 10 to 70 parts by weight of an ethylene/alkyl acrylate copolymer having up to about 30% by weight of an alkyl acrylate.

* * * *

EXHIBIT 9

THIS EXHIBIT HAS BEEN REDACTED IN ITS ENTIRETY

EXHIBIT 10

THIS EXHIBIT HAS BEEN REDACTED IN ITS ENTIRETY

EXHIBIT 11

JUL 22 '97 02:09PM SPALDING R.& D

P.2/6

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of MICHAEL J. SULLIVAN ET AL

Serial No. 08/631,613

Examinier: Mario, G.

Filing Date: 04/10/96

Group Art Unit: 3304

For: Improved Multi-Layer Golf Ball

Assistant Commissioner for Patents Washington, DC 20231

Sir:

DECLARATION OF MARK L. BINETTE UNDER 37 C.F.R. 1.132

- I. Mark L. Binette, hereby declare and say that:
- Lam a co-inventor of U.S. Application No. 08/831,813 and am employed as an associate scientist for Spalding Sports Worldwide.
- I understand that the claims of U.S. Application No. 08/631,613 have been rejected as being obvious in view of U.S. Patent No. 5,586,950 to Endo.
- 3. I formed 1 2 dozen golf balls in accordance with Comparative Example No. 2 of Endo '950. The balls of Comparative Example 2 appear to be the most similar of all of the Examples provided in Endo '950 to the subject matter claimed in U.S. Application No. 08/631,613. The balls which I produced are designated as Example 4 on Table 1 below. I also prepared 1 2 dozen golf balls with the same mantia layer composition as was used in Comparative Example No. 2 of Endo, but using a different type of outer cover layer. This set of examples is designated as Example 2 on Table

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- 1. Furthermore, I prepared a number of control examples, which are designated as Examples 1, 3, 5 and 6 on Table 1.
- 4. The cores for the balls of each example were molded and centerless ground to the appropriate size. The mantles used in Examples 1 4 were injection molded in a 1.83" injection mold. The mantles for the balls of Examples 5 and 6 also were injection molded. All cover molding was performed in an injection mold. The core and cover formulations referenced on Table 1 are set forth on Table 2.
- 5. As indicated above, the balls of Example 4 are replicas of Comparative Example 2 of Endo '950. These balls have an outer cover layer with a Shore D hardness of 57 when the hardness is measured on the curved surface of the ball, rather than on a plaque. Thus, the balls have a harder outer cover than is claimed in original claims 1 37 and in new claim 38 of the present application. I also note that the Endo specification at column 12, lines 35 40 indicates that the balls of Comparative Example 2 were rated as "X5," meaning that they were too soft and heavy and had inferior resilience. It is therefore clear that the balls which have a softer cover than that of Example 4 on Table 1 also would be considered "too soft" under the standards of Endo '950. Stated another way, Endo does not disclose or teach the soft multi-layer ball that is claimed in the present application.

For purposes of this declaration, "Shore C/D hardness" of a cover is measured generally in accordance with ASTM D-2240, except the measurements are made on the curved surface of a molded cover, rather than on a plaque. Furthermore, the Shore hardness of the cover is measured while the cover remains over the core. When a hardness measurement is made on a dimpled cover, Shore hardness is measured at a land erea of the dimpled cover.

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P.4/6

6. The balls of Examples 1, 2 and 5 fall within the scope of the invention which is claimed in the present application, as their outer cover layer hardness is 48 - 49. In contrast, the balls of Examples 3, 4 and 6 fall outside the scope of the claims of the present application, as the claims racite a Shore-D hardness value of 50 or less, or more preferably 48 or less.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 1-22-97

Ref: P-4628 - SPALD/164/US

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Mark L. Binette